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PHYSICS DEPARTMENT

COLLEGE OF CHEMISTRY AND PHYSICS

THE PENNSYLVANIA STATE UNIVERSITY

Technical Report
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CONTENTS

l-type Doubling in C_2H_2 and HCN [*]

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Abstract

A high resolution infrared grating spectrometer has been used to investigate l-type doubling of energy levels of the linear molecules C_2H_2 and HCN. Resolving power of 145,000 was obtained at 4200 cm^{-1} which permitted the resolution of the Q branch of $v_1 + v_5^1$ ($\Sigma^+ - \pi_u$) of C_2H_2 to $J'' = 6$. The difference between the $B' - B''$ value determined from the Q branch and the same quantity obtained from the P and R branches of this band yields a value of $q = 4.72 \times 10^{-3}$ cm^{-1}.

The doublet structure in the difference band $01^1 0 \to 01^1 2$ ($\pi - \pi$) of HCN has been resolved for $J'' \geq 6$ in the R branch and $J'' \geq 10$ in the P branch. This $\pi - \pi$ band is treated as two bands with slightly different molecular constants. Evaluation of rotational constants shows that different α values are obtained for the + and − components of these π states. The difference in frequency between lines of equal J'' in the $000 \to 002$ and $01^1 0 \to 01^1 2$ bands is shown to be a quadratic function of J''. The value obtained for q' was 7.68×10^{-3} cm^{-1}.

Introduction

The change in the B values caused by ℓ-type doubling in linear molecules has been observed and described by Herzberg.[1]

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1. G. Herzberg, Rev. Mod. Phys. 14, 219 (1942).

Making use of high resolution and precise methods of measuring wave length recently developed in this laboratory[2] it has been possible

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2. D. H. Rank, E. R. Shull, J. M. Bennett and T. A. Wiggins, (In Press).

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to investigate ℓ-doubling in linear molecules in more detail. It will be shown that some of the assumptions usually made in the analysis of $\pi \rightarrow \pi$ bands are not justified and that more constants are required to give an adequate description of these bands.

The spectrometer has been described completely elsewhere.[2] It is sufficient to state that an eight inch 15,000 lines/inch Bausch and Lomb plane transfer grating was used double-passed with ten meter optics. The signal from the Eastman PbS detector was fed into a Baird phase-sensitive amplifier. Uniform scanning of the spectrum was accomplished making use of a sliding wedge prism arrangement. The precision of relative frequency measurement of the lines in the P and R branches of the 4100 cm^{-1} band of C_2H_2 and the "hot" band lines of HCN at 6500 cm^{-1} is ± 0.005 cm^{-1}. The precision obtained in measurement of the lines of the Q branch of $\nu_1 + \nu_5^1$ of C_2H_2 and lines of the 002 band of HCN was considerably higher.

Resolution of 145,000 was obtained in the case of the Q branch of the C_2H_2 band. Theoretical resolution with the slit widths used was 175,000. The absorption tube had a length of 320 cm. It was necessary to reduce the pressure in the case of the acetylene band to 1.3 mm of Hg to achieve maximum resolution. The resolution obtained with the HCN ... ... was somewhat lower since it was necessary to use a pressure ... than desirable to develop the "hot" band with sufficient intensity.

Acetylene

The perpendicular band $v_1 + v_5^1 (\Sigma_g^+ \to \pi_u)$ of acetylene at 4092 cm^{-1} has been measured to show the difference between the B' values obtained from the Q branch compared to that obtained from the P and R branches. This effect of doubling has been observed and explained by Herzberg.[1] He has shown that due to the selection rules the π^- levels of the upper vibrational state are involved in the Q branch transitions while the π^+ levels are involved in the production of the P and R branches. With the resolution available it has been possible to resolve the Q branch so that a value for $B_-' - B''$ can be found, where B_-' denotes the constant for the π^- levels of the upper state. The Q branch of this perpendicular band is shown in Figure 1. Intensity alternation is shown with the anti-symmetric levels (odd values of J'') having the greater weight. Resolution to $J'' = 6$ is shown. It would require theoretical resolving power to resolve the $J'' = 5$ line.

If we neglect the effect of the D correction terms we can write the expression representing the frequencies of the Q branch as follows:

$$v = v_{0} - B_-' + (B_-' - B'')J(J+1) \qquad J \geq 0 \qquad (1)$$

A plot of the measured frequencies in this branch versus $J(J+1)$ is shown in Figure 2. Since the plot of this experimental data shows no trace of curvature it can be seen that the assumption regarding D is amply justified. The deviations from the least squares fit of the data are shown in the upper portion of Figure 2. The average deviation was found to be ± 0.002 cm^{-1}.

If we make the assumption that $D'=D''=D$, the expression for the frequencies of the lines of the P and R branches of this band becomes:

$$\nu = \nu_{o+} - (B'_+ + D) + (B'_+ + B'' + 2D)m + (B'_+ - B'' + 2D)m^2 - 4Dm^3 \qquad (2)$$

where $m = J + 1$ for the R branch and $-J$ for the P branch.

The frequencies of eight lines out to $J'' = 17$ in the P and R branches of this band were measured making use of the second order 1.22μ Fabry-Perot white line fringes as wave length standards. The measured lines were fitted to Equation 2 by least squares. The average deviation was ± 0.003 cm^{-1}. We have obtained the following molecular constants for this band expressed in cm^{-1}:

$B'' = 1.17658$ $\nu_{o+} = 4092.34$
$B^0_+ = 1.16952$ $\nu_{o-} = 4092.17$
$B'_+ = 1.17424$ $q^- = 4.72 \times 10^{-3}$
$D = 1.0 \times 10^{-6}$

These constants can be compared with previous work on acetylene. Herzberg[3] quotes a value of $B'' = 1.17692$ cm^{-1}. Bell and Nielsen[4]

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3. G. Herzberg, Infrared and Raman Spectra (D. Van Nostrand Co., 1945)p.398.

4. E. E. Bell and H. H. Nielsen, J. Chem. Phys. 18, 1382 (1950).

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obtained a value of $B'_+ - B'' = -0.0078$ compared with -0.00706 cm^{-1} obtained in the present investigation.

Hydrogen Cyanide

The difference band $01^1 0 \rightarrow 01^1 2$ ($\pi \rightarrow \pi$) associated with the $000 \rightarrow 002$ band of HCN has been observed under sufficient resolution to resolve the ℓ-doublets in the R branch for $J'' \geqslant 6$ and in the P branch for $J'' \gtrsim 10$. The lines of the $000 \rightarrow 002$ band of HCN have been measured recently in this laboratory by Yost[5] with a precision comparable to that obtainable in the

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5. E. L. Yost, M. S. Thesis, The Pennsylvania State College, June, 1953

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photographic infrared. The work of Yost showed that no rotational perturbations appeared in this band. B'' has recently been investigated with high precision.[6,7]

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6. D. H. Rank, R. P. Ruth and K. L. Vander Sluis, J. Opt. Soc. Am. 42, 693 (1952).

7. A. E. Douglas and D. Sharma, J. Chem. Phys. 21, 448 (1953).

We have measured 20 lines in the 002 band by the Method of Exact Orders.[2] These lines are listed in Table I and are marked with an asterisk. There is still probably a small systematic error in these measurements womewhat less than 0.010 cm^{-1} across the complete P branch. We shall assume the microwave B'' to be 1.47823 cm^{-1} and B' to be 1.45691 cm^{-1}, which at the present time are the most probable values of these constants. The remaining lines of the 002 band listed in Table I have been obtained by interpolation between measured lines. The frequencies of the lines of the 002 band thus determined were used as standards for measurement of the $\pi - \pi$ band lines. The results of these measurements are compiled in Table I.

Determination of q

On the basis of the theory presented by Douglas and Sharma[7] the frequency separation of the ℓ-doublets in a $\pi \rightarrow \pi$ band is given by:

$$\Delta\nu = q'(m^2 + m - 1) - q''(m^2 - m - 1) \qquad (3)$$

where $m = -J$ for the P branch and $J + 1$ for the R branch, $q' = B'_- - B'_+$ and $q'' = B''_- - B''_+$. Making use of the direct measurement of $q'' = 7.47 \times 10^{-3}$ cm^{-1} by Shulman and Townes[8] by microwave methods, the _____ side of the _____

6. R. G. _____ and ____. H. _____ , ____. ____. (7, 42? (1950).

side of Equation 3 can be calculated for each doublet. In Figure 3 we have plotted $\Delta\nu + q''(m^2 - m - 1)$ vs. $(m^2 + m - 1)$. The least squares treatment of this data yielded $q' = 7.76 \times 10^{-3}$ cm^{-1}. It was found necessary in making the plots in Figure 3 to consider the doublet separation to be negative in the P branch and positive in the R branch so that both plots would have the proper intercepts and equal slopes.

An alternate method of analysis of the ℓ-doublets is possible which should yield much more reliable values of $q' - q''$ than the above treatment. However, this second method does not give as precise an absolute value of the q's as is obtainable from the microwave measurements. We can express the separation of the ℓ-doublets to sufficient approximation by

$$\Delta\nu = (q' - q'')m^2 + (q' + q'')m \qquad (4)$$

A plot of the data using Equation 4 is given in Figure 4. The absolute value of q is determined by the absolute value of the doublet separations which can be subject to systematic error when close line pairs are involved. We have put the data to least squares using only the completely resolved

doublets, i.e. $\Delta \nu \geq .17$ cm^{-1}. From this analysis we obtain q" = 7.59×10^{-3} and q' = 7.80×10^{-3}. Even though the absolute value of q" does not agree exactly with the microwave q" we believe q' - q" is much more accurate than the value obtained from the use of Equation 3. From q' - q" determined from Equation 4 the most probable value of q' is 7.68×10^{-3} cm^{-1}.

The absence of intensity alternation in the doublets such as would occur in a symmetric molecule prevents a unique assignment of the lines of the doublets to a given energy level. However, on the basis of the required signs for the doublet separations noted above, it is concluded that the higher frequency component of the R branch is associated with the same energy level as the lower frequency component of the P branch and vice versa. To show this, an energy level diagram was constructed similar to the one shown by Herzberg[9] for a $\pi \to \pi$ band. The result is the

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9. See reference 3, p. 389.

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same as shown by Herzberg[10] for $^1\pi \to {}^1\pi$ bands of diatomic molecules.

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10. G. Herzberg, Spectra of Diatomic Molecules, 2nd Edition (D. Van Nostrand Co., New York 1950) p. 267.

This result differs from the diagram for linear molecules only in the order of the doublet components in the P branch. It is concluded that the π^+ (lower energy) levels are associated with the higher frequency doublet component in the P branch and the lower frequency component in the R branch; the π^- (higher energy) levels with the lower frequency doublet component in the P branch and the higher frequency component in the R branch.

Since as was noted above the energy levels are double in π states, we actually have two sets of rotational constants and effectively a $\pi \rightarrow \pi$ band is two bands which are almost identical. We shall call one of these bands π^+ and the other π^-. If we assume $D' = D''$ for these hot bands the frequencies of the band lines can be expressed by the following equation:

$$\nu_h = \nu_{oh} - (B'_h - B''_h) + (B'_h + B''_h + 4D_h)m + (B'_h - B''_h)m^2 - 4D_h m^3 \qquad (5)$$

A fit of the band lines by means of least squares was performed. The fit gave an average deviation of ± 0.007 cm^{-1}.

Douglas and Sharma[7] have pointed out that it should be possible to determine α_2 from the difference in frequency of "hot" and "cold" band lines (average frequency of λ-doublets) of the same J. The attempt of these authors to evaluate α_2 in this manner from the 003 band and its accompanying "hot" band was unsuccessful and perplexing. We have made an attempt to perform the same type of analysis as Douglas and Sharma on the 002 band and its accompanying hot band with even more perplexing results. Since our relative frequency measurements were considerably more accurate than those made in the photographic infrared, our scatter of points was much smaller than that obtained by Douglas and Sharma. The plot of the difference between the frequencies of the "cold" lines and the average frequency of the appropriate doublets versus m yielded a smooth curve instead of the straight line predicted by first order theory.

The difference between the frequencies for the same value of J in the "hot" and "cold" bands can be shown to be:

$$\nu_c - \nu_h = \nu_{oc} - \nu_{oh} + B'_h - B''_h + (\alpha' + \alpha'')m + (\alpha' - \alpha'')m^2 \qquad (6)$$

The quantities $\nu_c - \nu_h$ are plotted versus m in Figure 5 for the $+$ and $-$ hot bands and also for the average of the $+$ and $-$ bands.

The molecular constants for the π^+ and π^- bands have been determined applying least squares methods to the data using Equation 5 and Equation 6. In addition, the conventional $\Delta_2 F''$ method was used for the π^+ and π^- bands and also for the average of the two bands. The results are summarized in Table 2. The fifth figure beyond the decimal point has little significance and is carried as an inferior number. The agreement with the results obtained by Douglas and Sharma[7] for the 01^10 state average is excellent. It should be pointed out that our analysis shows unequivocally that the π^+ and π^- states yield a_2 values of a completely different order of magnitude. It also appears that the a_2 value for the 01^12 state is slightly larger than that for the 01^10 state.

We are indebted to Dr. A. E. Douglas of the National Research Council at Ottawa for pointing out a systematic error in our first measurements of this band and supplying us with his extensive $\Delta_2 F''$ values obtained from numerous "hot" bands in the photographic infrared. We are also grateful to Jean M. Bennett for performing a large part of the least squares calculations.

Table I.   Frequencies in vacuum wave numbers in two bands of HCN

m	ν_c (000 → 002)	ν_h ($01^10 - 01^12$) π^-	π^+	$\Delta\nu_h$
-26	6429.277*	-	-	-
-24	37.208*	-	-	-
-23	41.116*	-	-	-
-21	48.807*	-	-	-
-20	52.593	6413.691	6413.910	-0.219
-19	56.338*	17.422	17.632	.210
-18	60.046*	..	-	-
-17	63.712	24.791	24.982	.191
-16	67.335*	28.409	28.594	.185
-15	70.918	31.986	32.156	.170
-14	74.459*	35.529	35.679	.150
-13	77.958	39.031	39.183	.152
-12	81.415*	42.489	42.615	.126
-11	84.832	45.922	46.029	.107
-10	88.207	49.294	49.399	.105
- 8	94.832	6455.972		-
- 7	98.082	59.221		-
- 6	6501.290	62.414		-
- 5	04.457	65.586		-
- 4	07.582	68.716		-
- 1	16.704*	=		-
0	19.661	80.771		-
2	25.447	86.640		-
3	28.277	89.472		-
4	31.064	92.269		-
7	39.170	6500.455	6500.366	+0.089
8	41.787	03.085	02.974	.111
9	44.362	05.681	05.549	.132
10	46.893	08.263	08.107	.156
11	49.382*	-	-	-
12	51.828	13.254	13.050	.204
13	54.229*	15.679	15.456	.223
14	56.586	18.066	17.815	.251
15	58.901*	20.413	20.137	.276
17	63.400*	24.977	24.668	.309
18	65.585*	27.193	26.846	.347
19	67.726	29.359	28.997	.362
20	69.824*	-	-	-
22	73.891*	35.631	35.195	.381
23	75.859*	-	-	-
25	79.664*	-	-	-
27	83.301*	-	-	-

* Measured frequencies. The other frequencies in this band are computed.

Table II. Rotational constants of $01^10 \leftarrow 01^12$ bands in vacuum wave numbers determined by different methods.

π^+ Band

Constant	$\Delta_2 F''$	Eqn. (5)	Eqn. (6)
B''	1.47870	1.47868	-
B'	-	1.45788	-
a''	-0.00057	-0.00097	+0.00025
a'	-	-0.00045	-0.00006
ν_0	-	6480.807	6480.809

π^- Band

B''	1.48519	1.48503	-
B'	-	1.46444	-
a''	-0.00696	-0.00680	-0.00691
a'	-	-0.00753	-0.00746
ν_0	-	6480.810	6480.806

Doublet Average

B''	1.48194	1.48185	-
B'	-	1.46116	-
a''	-0.00371	-0.00363	-0.00333
a'	-	-0.00425	-0.00376
D''	3.40×10^{-6}	-	-

Q(1) calc. 6480.767
Q(1) obs. 6480.771

Captions for Figures

Figure 1. The Q branch of C_2H_2 at 4092 cm^{-1}. The line $J'' = 6$
is resolved showing resolution of 145,000.

Figure 2. Plot of frequencies in the Q branch of C_2H_2 versus $J(J+1)$.
The upper plot shows the deviations between the measured
frequencies and a least squares fit.

Figure 3. Splittings in the P and R branches of the $\pi \rightarrow \pi$ band of
HCN at 6481 cm^{-1}. The frequency difference between the
doublets is added to the quantity $q''(m^2 - m - 1)$ and the
sum plotted versus $(m^2 + m - 1)$. The separation in the P
branch is taken to be negative, and the R branch to be
positive.

Figure 4. Plot of the doublet separation $\Delta\nu/m$ versus m for the lines
of the $01^1 0 \rightarrow 01^1 2$ band of HCN. The points indicated by
X were not used in the determination of q.

Figure 5. The difference between frequencies in the $000 \rightarrow 002$ band
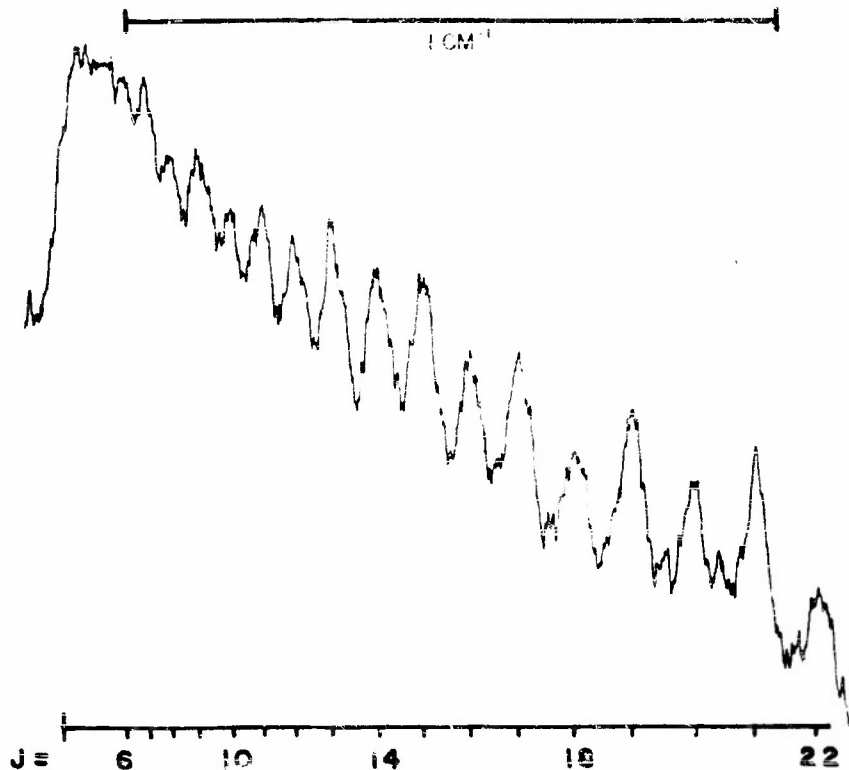and the $01^1 0 \rightarrow 01^1 2$ band of HCN are plotted versus m.

FIG. 1
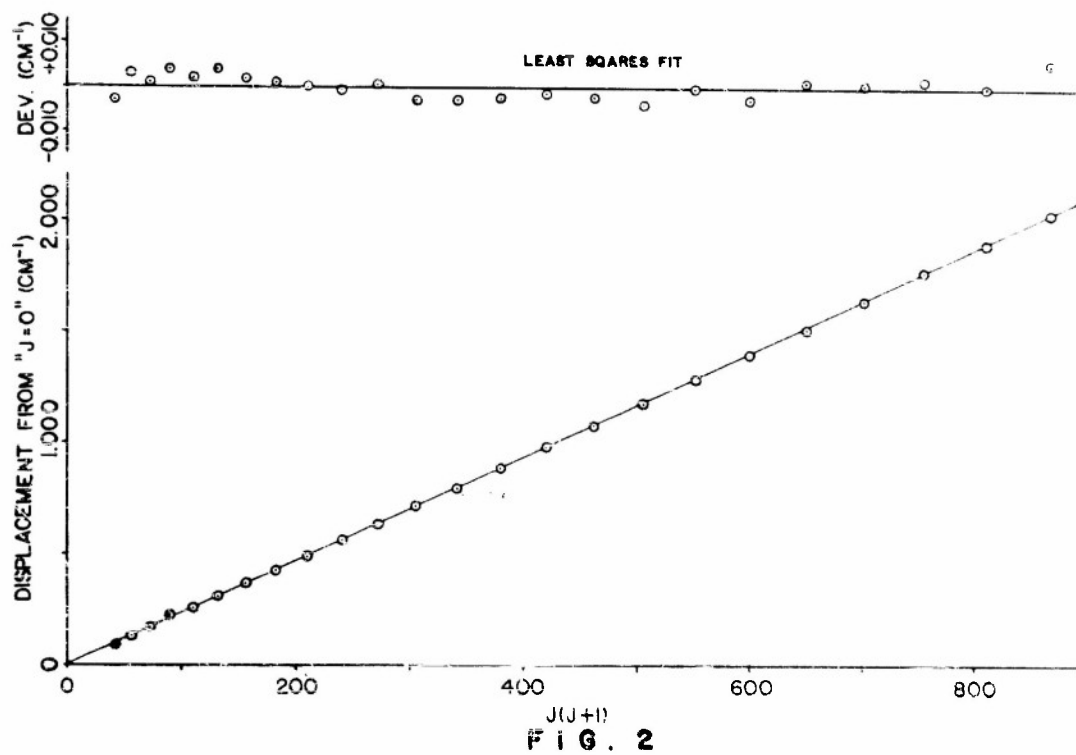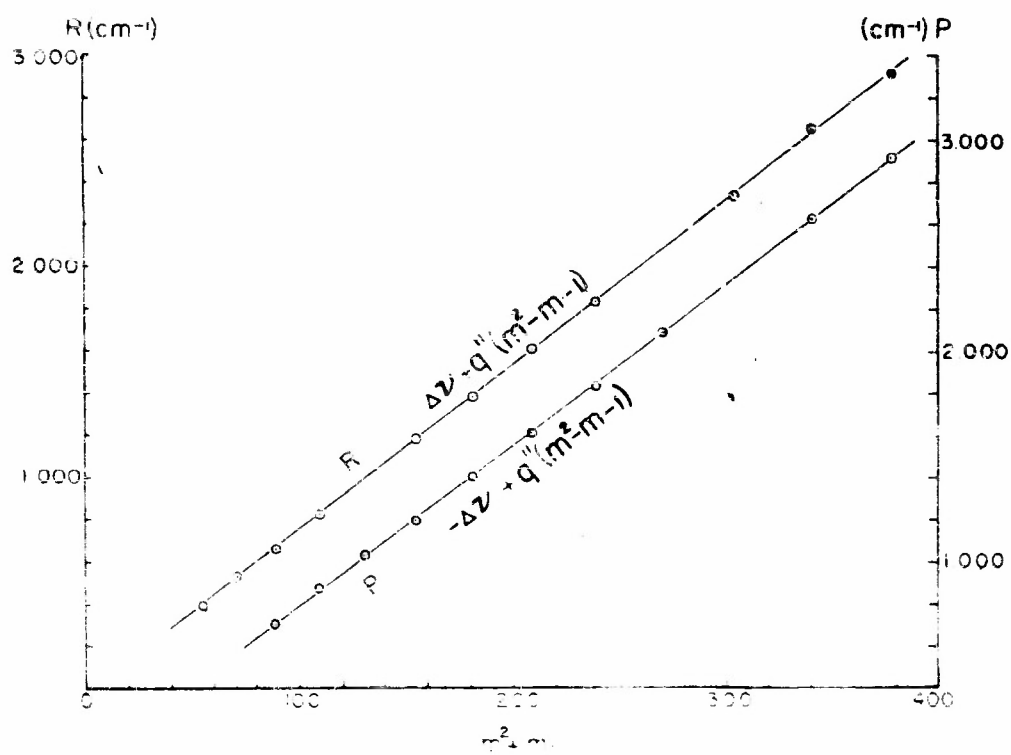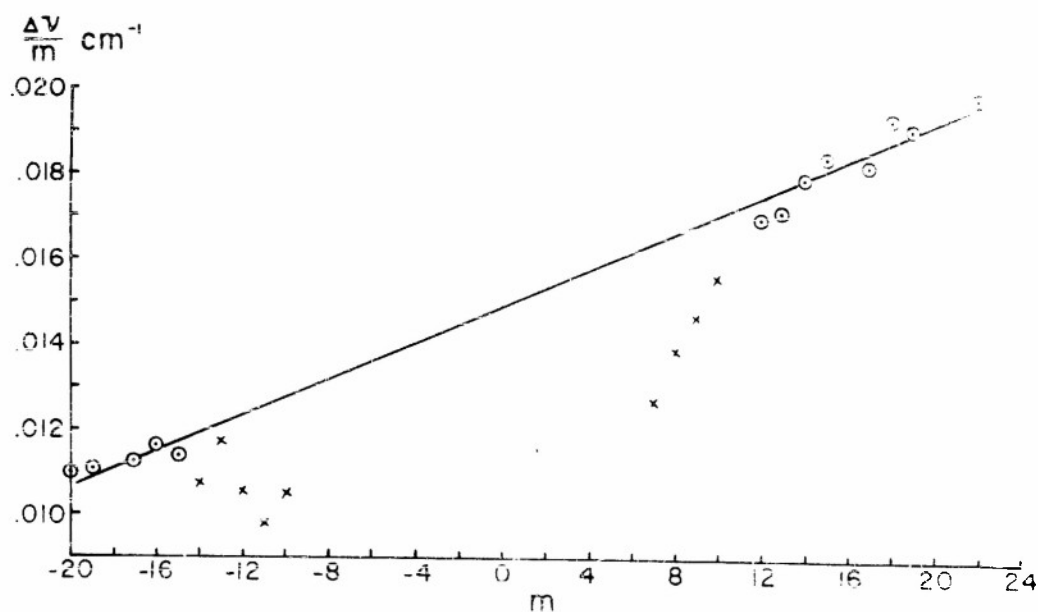

FIG. 2

FIG. 3
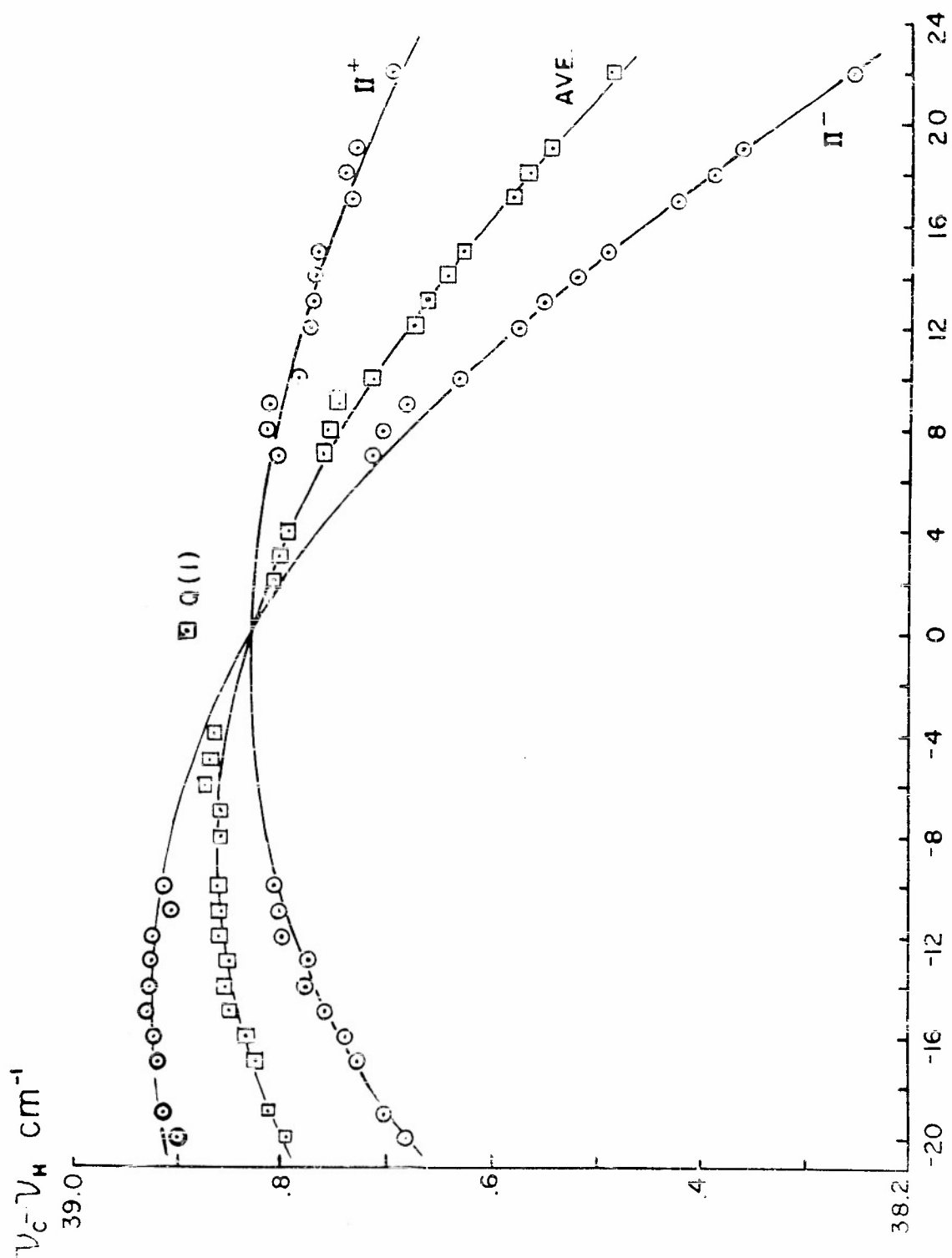

FIG 4

F I G. 5

Abstract

The infrared spectrum of C_3O_2 has been studied in the vapor phase from 2.2 to 20μ with a Perkin-Elmer double-pass spectrometer, and the Raman spectrum has been photographed in the liquid phase. A comparison of the Raman with the infrared spectrum shows definitely that the molecule has a center of symmetry as is required for the linear structure commonly assumed. However, the infrared spectrum can not be explained on the assumption of a linear model; the envelopes of the principal absorption bands as well as those of the weaker combination bands have the wrong shape. It appears rather that the oxygen atoms are bent out of line with the carbons in a plane zig-zag configuration. From the rotational structure of one of the combination bands the O-C-C angle is computed to be approximately 158°.

THE INFRARED AND RAMAN SPECTRA OF CARBON SUBOXIDE[*]

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Introduction

The carbon suboxide molecule has commonly been assumed to have a linear symmetric structure,[1] the two oxygen atoms lying at either end of the chain of three carbons. Results of earlier Raman[2] and infrared[3] studies of the molecule were not inconsistent with this assumption, which appeared to be supported also by the electron diffraction evidence.[4] The previous Raman work was carried out under far from optimum conditions; also the infrared absorption was obtained with the use of only a KBr prism for the entire range investigated, from 500 to 4500 cm^{-1}. Hence it was considered advisable to repeat these experiments with the superior spectroscopic equipment that has been developed since the original work was done. The data obtained in the present investigation are not entirely consistent with the linear model hitherto assumed for C_3O_2; it now appears that the oxygen atoms on the average are bent out of line with the three carbon atoms but in such a fashion as to preserve a center of symmetry. In more recent electron diffraction work,[5] reported after the present study was begun, the authors favor a linear model but admit the possibility of a non-linear one.

Experimental

Carbon suboxide was prepared by the pyrolysis of diacetyl tartaric anhydride at low pressure in a system similar to that used by Kobe and

Reyerson.[6] Vapors from the pot containing the anhydride, which was maintained at a temperature of 150° C, passed through a 14 mm quartz tube enclosed in a cylindrical furnace at a temperature of 700° C. A series of liquid air traps was used to separate the various products of the reaction, the C_3O_2 being vacuum distilled before removal from the system.

The Raman spectrum was taken in a prism spectrograph[7] with a dispersion of 19 A/mm at 4600 A; the sample tube was of about 12 ml capacity. With the first sample studied, the temperature was held at -80° C for an exposure time of eight hours. Polarization measurements were made on this sample by the method of polarized incident light.[8] Later a new sample was prepared and the experiment repeated with an exposure time of eleven hours at a temperature of -70° C. On each occasion the sample was vacuum distilled into the Raman tube.

Preliminary infrared measurements were made with a Perkin-Elmer Model 12-C spectrometer using NaCl and KBr prisms. An 8 cm pyrex cell with AgCl windows was employed after it was discovered that the vapor polymerized in a metal cell, yielding spurious absorption bands. Subsequently the infrared spectrum was remeasured with the Perkin-Elmer double-pass spectrometer, a LiF prism being used for the region above 2000 cm^{-1}.

Several attempts were made to obtain the photographic infrared spectrum of C_3O_2, in particular the combination of the second overtone of the strong infrared active fundamental at 2258 cm^{-1} with the Raman active fundamental at 2190 cm^{-1}. No spectrum was found with a 3 m path at a vapor pressure of about 60 cm, the dispersing element of the spectrograph being a 21-foot concave grating. A 2 m tube of the J.U. White type was constructed which made possible a path up to about 54 m. Utilizing a 5 m concave grating

a few weak lines representing the band in question were photographed and measured with third-order iron standards. Also photographs were taken with a Bausch and Lomb transfer plane grating and a 16-foot camera. With a vapor pressure as high as 71 cm on the silvered surfaces of the multiply reflecting mirrors were rendered useless in an hour's time by the action of the C_3O_2. When the vapor pressure was reduced to 50 cm, the freshly silvered surfaces deteriorated more slowly, but at such a rate as to make it impossible to obtain satisfactory exposures. With a much smaller vapor pressure, the resulting weaker absorption also yielded unsatisfactory plates.

Observed Spectrum

The original Raman spectrum of C_3O_2 obtained by Engler and Kohlrausch[2] showed five certain and four doubtful lines. The first Raman spectrum photographed in this investigation with an 8 hr exposure included 11 lines of which five or six could be called certain. However, when the experiment was repeated with a new sample, an exposure of 11 hours yielded only four lines, one of which is apparently an overtone of one of the others. The Raman measurements are presented in Table I. Three of the lines observed in the 8 hour exposure can be identified as due to methyl acetylene, which is known to exist in the sample (as well as acetylene) from the photographic infrared plates. Of the four lines obtained on both plates, the one at 577 cm^{-1} is depolarized, the others being polarized. The line at 828 cm^{-1} is very broad and comparatively diffuse.

The infrared spectrum reported here is in substantial agreement with that of Lord and Wright[3] as to the number and positions of the bands, allowance being made for the difference in precision of measurement possible with the two spectrometers. However, with the superior resolving power of

the Perkin-Elmer double-pass instrument, one can now distinguish the band
envelopes much more clearly. A trace of the infrared spectrum in Fig. 1
shows that the prevailing band type for carbon suboxide with the resolution
available consists of a strong central maximum. The principal exceptions
to this in the NaCl region include a band of medium intensity at 1122.5 cm^{-1}
with P-Q-R structure, and at slightly lower frequency a series of peaks of
varying intensity and separation. In the LiF region are found bands with
a central minimum at 2154.5 and 2386 cm^{-1} suggesting P-R structure and
another at 3335 cm^{-1} with a very weak central maximum between much stronger
side branches. The most informative band envelope in this region is that
at 2386 cm^{-1} in which two strong maxima are accompanied on the short wave-
length side by a set of weak maxima of fairly regular separation. (The
absence of these maxima on the long wavelength side of the 2386 cm^{-1} band
may be ascribed to the overlapping of this region by atmospheric CO_2 and
by the very strong fundamental band at 2258 cm^{-1}.) The band at 4445 cm^{-1}
is possibly also of this type, the resolution of the spectrometer not
being great enough to separate the weak maxima. In Table II are given
the measurements of the infrared bands along with those of Lord and Wright.

Discussion of the Spectrum

Herzberg[9] has discussed three possible models for carbon suboxide:
(I) $O=C=C=C=O$, (II) $O{\nwarrow}C=C=C{\searrow}O$, (III) $O{\nwarrow}{}^{C}{\searrow}{}^{C}{\searrow}O$ belonging
to the point groups $D_{\infty h}$, C_{2h}, and C_{2v}, respectively, and attempted vibra-
tional assignments for Models I and III, his assignments for I differing
in part from those of Lord and Wright. For models I and II, which have a
center of symmetry, only three of the fundamentals are Raman active, while
for model III all nine fundamentals are Raman active and eight are infrared
active as well. From the Raman spectrum alone, which can best be analyzed

as consisting of three fundamentals and one overtone, it would appear that model III can be eliminated as a possible structure for carbon suboxide. This conclusion is strengthened by a comparison of the Raman and infrared spectra, for it turns out that there are no coincidences between them. A further reason for believing that the molecule has a center of symmetry is that there are no first overtones of the infrared fundamentals although the band at 1666 cm^{-1} can be reasonably interpreted as a second overtone. Likewise there are no binary combinations of infrared fundamentals but numerous binary combinations of infrared and Raman active vibrations.

It is not possible to choose between models I and II on the basis of the Raman spectrum. For the linear model the Raman lines at 2190 and 828 cm^{-1} would be assigned to the two symmetric stretching modes of species Σ_g, while for the bent model II these lines would be of species A_g. The line at 577 cm^{-1} should be due to the bending mode π_g for the linear model and A_g for the zig-zag one. The polarization data (see Table I) might seem to favor model I for which this last Raman line should be depolarized, whereas all three lines should be polarized for model II. However, since for a totally symmetric vibration the degree of depolarization may vary between 0 and 6/7, model II cannot be called inconsistent with the Raman spectrum. There remains to consider the evidence provided by the envelopes of the infrared bands.

Assuming the linear model there are four infrared active fundamentals, two of which should be represented by parallel bands with a separation of about 11 cm^{-1} between the P and R branches, and two by perpendicular bands with P, Q, and R branches. The most probable assignments for these would be the strong bands at 2258 and 1570 cm^{-1} for the two stretching vibrations (of species Σ_u) and those at 635 and 551 cm^{-1} for the bending vibrations (π_u).

However, none of these bands has the required envelope; in fact, they all
show just a strong central maximum with no side branches. All of the other
bands shown in Fig. 1 with the exception of those at 779.5 and 1040 cm^{-1}
could be accounted for as arising from these four fundamentals, nearly all
being combinations of the infrared with the Raman active fundamentals.
Aside from the previously mentioned band at 1666 cm^{-1}, which appears to
be the second overtone of the infrared active fundamental at 551, and the
band at 3335 cm^{-1}, which is probably a combination of the first overtone
of this same fundamental with the highest frequency fundamental at 2258 cm^{-1},
the remaining bands of the infrared spectrum can be explained as binary
combinations involving one Raman and one infrared fundamental.

An examination of the band envelopes which have a more complicated
structure than just a central maximum brings out the following discrepancies.
The only one which shows definite PQR structure - at 1122.5 cm^{-1} - is a
combination of the two bending modes at 577 and 551 and should consequently
be of species Σ_u with P and R branches only. The band at 2154.5 cm^{-1},
which apparently has P and R branches with a separation of 14 cm^{-1} is
presumably due to a combination of the 577 Raman active vibration with
the infrared band at 1570 cm^{-1} and therefore of species π_u. The band at
3335 cm^{-1}, being a combination of the fundamental 2258 and the first over-
tone of 551 would be of species Σ_u, and here we have the proper band
contour if we assume that the weak central maximum is due to an impurity
in the sample, namely methyl acetylene. However, the P and R branch
separation of the P and R maxima is about 23 cm^{-1}. Furthermore this band
has structure on the short wavelength side which could not possibly arise

from a linear molecule. In view of all this evidence it seems necessary to abandon the assumption that carbon suboxide has a linear structure.

There remains to consider Herzberg's model II. It is interesting to note that this type of structure was recently proposed for an excited electronic state of the normally linear molecule acetylene by King and Ingold[10], who called it a "plane centro-symmetric zig-zag." This model for carbon suboxide requires in addition to the three Raman active fundamentals of species A_g mentioned above six infrared fundamentals, four of them in the plane of the molecule (B_u) and two out of the plane (A_u). It has already been shown that this model is consistent with the observed Raman spectrum. As for the infrared spectrum, it may be noted first that the four vibrations of species B_u may be assigned to the same four bands considered above as fundamentals for the linear model. Since the model now under discussion is a slightly asymmetric top, the difficulty about the contours of these fundamentals is removed. The two infrared bands at 779.5 and 1040 cm^{-1} which could not readily be accounted for on the linear model can now be assigned as the A_u vibrations. The first of these two has been resolved into four rather weak maxima with an average separation of about 5 cm^{-1}. The other band is not so clear cut. It appears to consist of two maxima of medium intensity at 1015 and 1025 cm^{-1} and three weaker ones at 1055, 1068 and 1075, with two other barely resolved shoulders between these two groups at 1033 and 1045 cm^{-1}. Under the available resolution it is not clear whether this absorption represents only one band or more than one, and a further complication may arise from the fact that one of the weaker fundamentals of methyl acetylene is found in this same region. In view of these uncertainties the band is here given a wave number of 1040, this being approximately the center of the absorption. The weak absorption of the 779.5 cm^{-1} funda-

mental may be explained thus: the vibration is believed to involve an out-of-plane motion of the two C-O groups against the central carbon with a consequently small change of dipole moment. A qualitative check on the assignment of these two fundamentals is provided by the fact that they should be pure perpendicular vibrations with no parallel component and this seems substantiated by the absence of the strong central absorption noted elsewhere in the infrared spectrum. A schematic representation of the vibrational modes for the zig-zag model is given in Fig. 2.

The fine structure on the short wavelength side of the band at 2386 cm^{-1} has an average separation of about 5.5 cm^{-1}. This structure may be interpreted as due to the perpendicular component of a hybrid band, the parallel component being represented by the strong central maxima. If this interpretation is correct, the band in question provides the strongest kind of evidence for the non-linearity of carbon suboxide. The similar structure on the long wavelength side of the 3036 cm^{-1} band, which has an average separation of about 9.5 cm^{-1}, is almost certainly due to the v_6 band of methyl acetylene, as the positions of the individual peaks check well with those reported in some recent work at higher resolution by Boyd and Thompson.[11] The irregularly spaced structure on the short wavelength side of this band has an average spacing of 13 cm^{-1} and may be due to a combination of the perpendicular band at 1040 with the Raman band at 2190 cm^{-1}. Owing to the above mentioned uncertainties with regard to the 1040 cm^{-1} band, this assignment is merely tentative. The unresolved background at the high frequency end of this structure is no doubt due to the acetylene in the sample, but the eight or nine partly resolved weak maxima cannot readily be attributed to some other impurity. In Table II are found the assignments for the infrared spectrum along with the earlier data of Lord and Wright.

On the basis of force constant calculations, Engler and Kohlrausch[2] postulated a low ifrequency fundamental at about 200 cm^{-1}. From the analysis of the infrared spectrum given above it appears that the assumption of such a frequency is unnecessary. Recently an examination[12] of the far infrared region of the carbon suboxide spectrum by the residual ray method has indicated weak absorption at 192 and 161 cm^{-1}. This is undoubtedly the difference band $\nu_2 - \nu_8$. A somewhat stronger difference band should be found near 275 cm^{-1} for $\nu_2 - \nu_9$, but apparently this region was not investigated.

As mentioned above two impurities in the sample of carbon suboxide used in this study that have been positively identified are methyl acetylene and acetylene. The $3\nu_1$ and $3\nu_3$ bands, respectively, of these two molecules were found in the photographic infrared with the rotational structure well resolved. In the near infrared region, the fundamental ν_5 of acetylene was observed as was also ν_3, the latter being overlapped by suboxide bands. A number of the fundamentals of methyl acetylene appeared including ν_1, ν_3 and ν_6; ν_9 would be completely covered by the 635 cm^{-1} band of carbon suboxide, but $2\nu_9$ may be present. The possibility[5] that ketene may occur as an impurity in carbon suboxide produced by pyrolytic reaction could not be verified in this infrared study; however, the stronger infrared bands of ketene lie near regions of carbon suboxide absorption and may be obscured. In the first Raman plate, the line at 1127 cm^{-1} may be the ketene line reported by Kopper[33] at 1130 cm^{-1}, but if this is so it is not clear why the almost equally strong line at 2950 cm^{-1} was not observed. Since the doublet of medium intensity reported by Lord and Wright at 909-889 cm^{-1} was not found in this investigation, it is possibly an impurity in their sample. The same inference may be drawn concerning the group of bands

they observed at 1760, 1850 and 1980 cm^{-1}, to which there corresponds in the present study only a very weak absorption near 1770 cm^{-1}.

Discussion of the Molecular Constants

As pointed out by Lord and Wright,[3] if the carbon suboxide molecule is linear it must have a moment of inertia of about 390×10^{-40} g cm^2, and this would give rise to a separation between the P and R branch maxima of a parallel band of about 11 cm^{-1}. Their failure to observe such a band was attributed to the low resolving power of their spectrometer. Since the Perkin-Elmer spectrometer employed in the present study can resolve bands separated by one wave number or a little less in the neighborhood of 2200 cm^{-1}, the failure to observe any splitting at all in the 2258 cm^{-1} band might alone be taken to indicate the non-linear structure of the molecule. The combination bands $v_2 + v_7$ and $v_3 + v_7$ on either side of the fundamental v_6 do exhibit a splitting suggestive of P and R branch envelopes, the separation of the maxima being 23 and 14 cm^{-1} respectively. This latter value is however extremely dubious because the position of the supposed P branch of the band coincides with that of a strong band of methyl acetylene, and also the strongest infrared band of ketene falls in this same region. As pointed out above, the strong maxima of the 3335 cm^{-1} band have a separation of about 22 cm^{-1}, which agrees well with the value observed for the band at 2366 cm^{-1}.

On the short wavelength side of the $v_2 + v_7$ band the group of weak subsidiary bands ranging from about 2440 to 2490 cm^{-1} has an average separation of about 5.5 cm^{-1}. Taking this band envelope to represent a hybrid band of a slightly asymmetric top, this separation to a first approximation is given by $2(A'-B')$. Since the value of B (or C) for carbon suboxide is of the order of .07 cm^{-1}, we can compute a value of A' from this band of about 2.7 cm^{-1} and I_A as 10.4×10^{-40} g cm^2. The most recent electron

diffraction measurements of carbon suboxide by Mackle and Sutton[5] give the
C-C and C-O distances as 1.23 and 1.19 A respectively. Applying these
values to the centro-symmetric zig-zag model discussed above, which seems
required from the spectrographic evidence, we obtain a value for the O-C-C
angle of 158°. While these authors do not consider this model, they do
discuss the possibility of a non-linear model of point group C_{2v} (Herzberg's
model III). For such a structure they conclude that the minimum value of the
O-C-C and C-C-C angles consistent with their data is 170^c for each angle.
A comparison of the spectroscopic and electron diffraction data can be made
even though two different models are involved by computing the displacement
of the oxygen atom from the C-C-C axis for the centro-symmetric model. For
an angle of 158° this distance is .44 A. From the electron diffraction
data the corresponding distance would be .43 A. Even though the electron
diffraction values quoted here represent only one interpretation of the
data (Mackle and Sutton prefer a linear model), the agreement with the
spectroscopic data is noteworthy.

The evidence on molecular structure that can be obtained from the two
bands in the NaCl region here assigned to the A_u vibrational species is less
satisfactory than that just discussed. In the 1040 cm^{-1} band the apparent
separation of the peaks ranging from 6 to nearly 15 cm^{-1} with an average
value of 10 may be due either to incomplete resolution or the presence of
an impurity. The four partly resolved peaks in the weak band at 789.5 cm^{-1}
have an average separation of nearly 5 cm^{-1}, and since this is only a
little less than that found in the combination band at 2386 cm^{-} it would
seem to provide some support for the structural analysis given above.

The photographic infrared work yielded no results that would provide
definite information about the structure of carbon suboxide. The only
conclusions that can be drawn from the few weak lines obtained is that

there was nothing to indicate a linear structure for the molecule and a slight suggestion that the spectrum could be due to an asymmetric top. It is hoped in the future to study the partly resolved bands which give some insight into the structure of carbon suboxide under higher resolution.

Table I. Raman spectrum of carbon suboxide

ν_{vac}	Description[a]		Assignment	Engler and Kohlrausch
cm^{-1}				cm^{-1}
577	m.	Dep.	ν_3	586
828	v.s., b.	P.	ν_2	843
1154	w.	P.	$2\nu_3$	1176
2190	s.	P.	ν_1	2200

Spurious or doubtful lines on first Raman plate: 335 (v.w.)
(Me Ac); 519 (w.); 1084 (v.w.); 1127 (m.) (ketene ?); 1381 (w.)
(Me Ac); 1642 (v.w.); 2132 (v.w.) (Me Ac).

[a] Abbreviations: v.s., s., m., w., v.w., b., Dep., P. - very
strong, strong, medium, weak, very weak, broad, depolarized,
polarized, respectively.

Table II. Infrared spectrum of carbon suboxide from 2.2 to 20 μ.

ν_{vac}(obs) cm^{-1}	Intensity[a]	Assignment	ν_{vac}(calc)[b] cm^{-1}	Lord and Wright cm^{-1}
				544
551	v.s.	ν_9		557
635	s.	ν_8		637
779.5	w.	ν_5		779
				889
				909
1040	m.	ν_4		1024
1122.5	m.	$\nu_3 + \nu_9$	1128	1126
1215.5	m.	$\nu_3 + \nu_8$	1212	1225
1375.5	v.w.	$\nu_2 + \nu_9$	1379	1387
				1470
1570[c]	s.	ν_7		1570
1666[c]	m.	$3\nu_9$	1653	1670
1770[c]	v.w.			1760
				1850
				1980
2154.5	s.	$\nu_3 + \nu_7$	2147	2190
2258	v.s.	ν_6		2290
2386[c]	s.	$\nu_2 + \nu_7$	2398	2410
2670	w.	$\nu_7 + 2\nu_9$	2672	
2738	w.	$\nu_1 + \nu_9$	2741	
2828	w.	$\nu_1 + \nu_8$	2825	
2840	w.	$\nu_3 + \nu_6$	2835	
3086	s.	$\nu_2 + \nu_6$	3086	3150
3335	m.	$\nu_6 + 2\nu_9$	3360	3380
3756[c]	s.	$\nu_1 + \nu_7$	3760	3790
3857[c]	w.	$\nu_1 + 3\nu_9$	3856	
4445	m.	$\nu_1 + \nu_6$	4448	4590

a   Abbreviations: v.s., s., m., w., v.w., = very strong, strong, medium, weak, very weak, respectively.

b   Neglecting effect of anharmonicity.

c   Band obscured or distorted by atmospheric absorption.

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LIMITATION TO THE PRECISION OF MOLECULAR CONSTANTS DETERMINED WITH A

DIFFRACTION GRATING

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Harrison, Davis and Robertson[1] have recently discussed the measurement of wavelength with gratings, echelles and interferometers. These authors have shown that due to ruling errors precision of wavelength measurement much in excess of 1 part in 10^6 is not to be expected for diffraction gratings. The spectroscopic literature has shown very extensively the unreliability of gratings to produce wavelengths with a precision much in excess of 1 part per million.

Recently[2] we have obtained measurements which give some quantitative idea of the effect of this lack of grating precision upon molecular B values obtained from gratings.

If we specify the inability of a diffraction grating to measure a wavelength correctly by $k = \Delta\lambda/\lambda$ the error in the frequency of the measured line will be $d\nu = -k\nu$. The maximum error introduced into a $\Delta_2 F$ from this grating error will be $\pm 2k\nu$.

It is necessary to measure a relatively large number of band lines to obtain B values for molecular states since D, the centrifugal correction, must be determined simultaneously with the determination of B. In the complete measurement of a band it is certain that the worst situation with regard to the uncertainty of wavelength measurements is highly improbable. Since the intensity of the band lines will vary from $J = 0$, reach a maximum at some J value and decrease to some value at maximum J, the strict treatment of this problem becomes very complex.

It is quite certain that the wavelength uncertainty from the grating error will be a function of the line intensity.

We can assume to a first approximation that the B value will be in error due to grating imperfections by an amount related to the maximum error introduced into the largest measured $\Delta_2 F$.

In the above mentioned approximation we can write

$$\frac{\Delta_2 F_t + d\Delta_2 F_t}{4(J+1/2)} = B_t \pm \frac{k}{2(J+1/2)} = B_t \pm dB \qquad (1)$$

where B_t is the true B value, J the maximum J measured and dB the error introduced into B due to the inability of the grating to measure wavelength precisely.

Inspection of equation 1 shows that using gratings having identical k, dB decreases linearly with wavelength for constant J. Furthermore the long waves are even more advantageous since the increased absorption for bands at longer wavelengths allows higher J values to be reached.

The strictly interferometric measurements of Rank, Shearer and Wiggins[2] for B_{000} of HCN yield a value for this constant completely consistent with all values of the velocity of light determined by the modern optical and microwave methods.

The earlier grating measurements of B_{000} of HCN by Rank, Ruth and Vander Sluis yielded a value of B_{000} larger by $(dB = 7 \times 10^{-5})$. These grating measurements were made with one of the most perfect gratings in existence and calculation from equation 1 shows that k for this grating is approximately 2.5×10^{-7}. Previous to the work of Rank, Ruth and Vander Sluis[3] attempts were made to measure B_{000} for HCN with a plane grating which was much more imperfect than the "Tuxedo" grating. The dB obtained was -3×10^{-4} which shows a k for this grating of 10×10^{-7}

It seems rather certain that the better gratings will have a k which varies between 2 and 5×10^{-7} for different gratings, which seriously affects the apparent precision of B values determined in the photographic infrared and of course becomes worse when shorter wavelengths are used. Thus in the photographic infrared in addition to the statistical probable error due to the scatter of the experimental points, the B values determined by a grating are likely to be in error by an additional 1×10^{-4} or greater due to the imperfections of the grating itself.

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PRECISION DETERMINATION OF THE VELOCITY OF LIGHT DERIVED FROM A BAND

SPECTRUM METHOD II *

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Abstract

The rotational constant B_{000} for HCN has been measured using the Method of Exact Orders for the 002 infrared rotation vibration absorption band. The value obtained is 1.47823_5 cm^{-1}. Combined with the microwave measurements by Nethercot and Klein of the same constant in pure frequency units, a value for the velocity of light, $c = 299789.8 \pm 3.0$ km/sec., is found. The change in the apparent thickness of the Fabry Perot interferometer with wave length due to the phase shift in the ZnS, MgF_2, ZnS coated plates is discussed and the experimental results compared with the calculated values. The rotational constants $\alpha_3 = 0.01003_4$ and $\gamma_{33} = 0.00018_3$ cm^{-1} were also obtained with the aid of other interferometric results.

The Method of Exact Orders which we have recently described[1] makes possible the determination of molecular constants with a precision hitherto unobtainable in optical spectroscopy. In the present work we have redetermined B_{000} for HCN in order to determine the velocity of light by the band spectrum method described by Rank, Ruth and Vander Sluis.[2]

In our preliminary work with the Method of Exact Orders a wave length sensitivity in excess of 1 part in 20 million was demonstrated. However, considerable difficulty was encountered because of the change in length of the interferometer spacer with temperature. In addition, the PV work accomplished in changing the air pressure during the "tuning" process produced deformation of the glass plates of the etalon, which is equivalent to a change of the etalon spacer. We have largely rectified the above mentioned difficulties by replacing the glass interferometer plates by plates of fused quartz, and also replacing the brass barrel of the etalon by a barrel constructed completely of invar.

Absorption measurements were made using a path length of HCN gas of three meters. The pressure of the gas was regulated so as to yield tuned patterns similar to those shown in Figure 2 of our previous paper.[1] The pressure used in these measurements varied between the limits of 1 to 10 mm of Hg of HCN gas. HCN is a notorious substance with regard to pressure broadening of its spectrum lines. We have not been able to detect any wave length shift of the HCN lines with pressure despite the sensitivity of our method. For some reason, the cause of which we are not completely certain, the fringes produced by our apparatus are slightly asymmetric. This asymmetry produces a pseudo small wave length shift if measurements are made at widely different absorption levels. Thus it is necessary to compare

"tunes" at approximately the same percentage absorption to obtain the most precise measurements of wave length intervals.

Determination of Phase Changes

The quartz interferometer plates were coated with triple-layer dielectric films of ZnS, MgF$_2$, ZnS of a $\lambda/4$ thickness at 17,250 Å. Since no precise absolute wave lengths are known in this region of the spectrum the Method of Exact Orders can not be used for determining the integral order of the interferometer. We have calibrated the integral order of the spacer by making use of second order neon lines using the method of exact fractions as described in our former paper.[1] Phase change on reflection which occurs with the dielectric films is large and varies with wave length. Fortunately the variation of the phase change with wave length in these films can be calculated with considerable precision making use of explicit formulae given by Leurgans[3] as derived from electromagnetic theory. Making use of the variation of phase with wave length as calculated, corrections are applied to the observed fractional orders so that the integral order of the etalon can be chosen using the conventional method of exact fractions.

We can determine the phase change versus wave length curve experimentally to higher precision using the method described in our previous paper.[1] This method involves obtaining the integral plus fractional orders for a number of different wave lengths using two different interferometer spacers. We have used a 13.19 and 5.95 mm spacer for the phase determination. The longer spacer was used for making the frequency measurement on the band lines. The ratios of these measurements made with the two spacers using the Method of Exact Orders can be used to

derive the variation of phase with wave length for the interferometer plates
being used.[1] The ratios obtained are plotted versus wave length in Figure 1.
In Figure 2 the theoretically and experimentally determined phase shift
has been plotted versus wave length. The agreement between theory and
experiment is very satisfactory since uncertainties in the film constants
(thickness and indices) might well account for the slight differences
observed. In any event the correction which must be applied in the
present work is small since the interval of wave length covered in our
measurements is only about 350 Angstroms. The magnitude of the phase
shift versus wave length correction can be expressed as amounting to
about 35 km per second in the velocity of light determination, in a
direction so as to make uncorrected measurements yield a value of c
too small.

Determination of Molecular Constants

In the absence of perturbations the frequencies of the lines in a
rotation vibration band of a linear molecule are given by the well
known expression

$$\nu = \nu_o +(B'+B'')m + (B'-B''-D'+D'')m^2 -2(D'+D'')m^3$$
$$-(D'-D'')m^4 \ldots \tag{1}$$

where ν_o is the band origin and B and D have their usual significance.
m takes positive integral values for R branch lines and negative integral
values for P branch lines. We can state as a result of our work that no
perturbations in the lines of the 002 band of HCN occur which are of a
magnitude greater than a few ten thousandths of a wave number, which is
the limit of our precision.

The following four equations express relationships which are useful

for determining the constants of (1) above.

$$R(J-1) - P(J+1) = \Delta_2 F''(J) = (4B''-6D'')(J+1/2) - 8D''(J+1/2)^3 \qquad (2)$$

$$R(J) \quad - P(J) \quad = \Delta_2 F'(J) = (4B'-6D')(J+1/2) - 8D'(J+1/2)^3 \qquad (3)$$

$$R(J-1) + P(J) \quad = \nabla_+(J) = 2\nu_0+2(B'-B''-D'+D'')J^2-2(D'-D'')J^4 \qquad (4)$$

$$R(J-1) - P(J) \quad = \nabla_-(J) = 2(B'+B'')J-4(D'+D'')J^3 \qquad (5)$$

For the purpose of the determination of the velocity of light by
the band spectrum method it is only necessary to determine the con-
stants B'' and D'' of Equation 2. Experimentally this simply involves the
determination of the frequency intervals of the line pairs designated
by Equation 2. The measurement of $R(J-1) - P(J+1)$ however involves
line pairs of considerable intensity difference especially at the large
values of J which are necessary for precise evaluation of the molecular
constants. When measurements of intervals are made on lines of considerably
different intensity the precision is much reduced under practically all
circumstances. In the present case with our method this error would be
particularly vicious because of the slight fringe asymmetry.

Inspection of Equation 3 will show that B' and D' can be obtained
by the measurement of line pairs of almost identical intensity. Equation
4 shows that B'-B'' and D'-D'' can also be obtained from line pairs
having nearly the same intensity. Further reflection will show that
Equation 4 yields one more decimal place for (B'-B''-D'-D'') than is
obtainable for B' from Equation 3 when high values of J are used. It
can be seen that $R(J-1) + P(J) - 2\nu_0$ increases proportionally to J^2 while
$R(J) - P(J)$ increases proportionally to $J + 1/2$. This favorable situa-
tion with regard to the $\nabla_+(J)$ plot can be strictly taken advantage of
with the interferometric method. From the preliminary measurements of
Douglas and Sharma[4] and Yost[5] the band origin of the 002 band has been

for the purposes of this investigation set by definition as 6519.6508 cm^{-1} in vacuo. Douglas and Sharma quote a value of 6519.65 cm^{-1} and Yost's value is 6519.68 cm^{-1}. The defined v_o yields a value of 6516.7043 cm^{-1} for $P(1)$ when combined with the known preliminary value of B''. $P(1)$ is then used for standardizing the interferometer and measurements of the band lines thus are made interferometrically with reference to the band origin. Likewise it can be seen that a constant determined from Equation 5 has less than half the precision of one determined from Equation 2 or 3. Calculations show that an absolute error in the band origin frequency will cause an absolute error in the largest $\Delta_2 F'$ of 2.3×10^{-4} cm^{-1} for each 0.01 cm^{-1} absolute error in the band origin. Thus each 0.01 cm^{-1} error in band origin absolute value will cause an error in c of 0.46 km/sec. We feel reasonably certain that the absolute value of v_o we have chosen is correct to ± 0.02 cm^{-1}.

Because of the much more favorable experimental procedure the major effort in this research was expended on the measurement of line pairs yielding $\Delta_2 F'(J)$ and $\nabla_+(J)$. Measurements were also made on $\Delta_2 F''(J)$ but as expected the scatter was much greater which would give them little statistical weight compared to the other measurements. The data were treated to least squares in the manner described by Rank, Ruth and Vander Sluis.[2] The results of the least squares treatment are given in Table I.

The smallness of the residuals shows that it would serve no useful purpose to include the conventional graphic plots since the points lie so close to the straight line that on the scale usually printed the scatter would not be apparent. $\Delta_2 F''(J)$ results treated to least squares yielded $B'' = 1.47825$ and $D'' = 3.01 \times 10^{-6}$. However, these results have

little statistical weight since the scatter of the points is much greater than the results given in Table I. We shall quote as our final result the values of the constants derived from Table I in cm^{-1} in vacuo.

$$B' = 1.45707_3 \qquad\qquad D' = 2.89_2 \times 10^{-6}$$
$$B'' = 1.47823_5 \qquad\qquad D'' = 2.97_5 \times 10^{-6}$$

Determination of the Velocity of Light

When we combine our result for B'' with the newly remeasured 0-1 transition in the microwave spectrum by Nethercot and Klein,[6] i.e, $B'' - 2D'' = 44,315.800 \pm .010$ mc/sec., we obtain $c = 299,789.8 \pm 3.0$ km/sec. The value of B'' microwave is $44,315.978 \pm .011$ mc/sec. when the D'' correction is made by means of our newly determined D'' value.

Since our measurements are made essentially with the interferometer in vacuo no appreciable error is involved due to uncertainties in the index of refraction of air. $(\mu-1)$ for air is made use of only to determine the fractional order and we must use only from 1% to 20% of this quantity for our purpose depending on the fractional order. We have used our recent determination[1] at 1.65 μ as the value of $(\mu-1)$ corrected by means of the dispersion formula of Barrell[7] for the proper wave lengths.

The probable error can be considered to be derived from the following sources:

$$\text{Microwave } \nu = \pm 0.10 \text{ km/sec.}$$
$$\text{Absolute Value of Band Origin} = \pm 0.90 \text{ km/sec.}$$
$$\text{Phase Change vs. } \lambda = \pm 1.00 \text{ km/sec.}$$
$$\text{Statistical} = \pm 1.00 \text{ km/sec.}$$

We have included in Table II the frequencies of the lines of the 002 band of HCN calculated from the final values of the molecular constants. We have only tabulated lines which were used to derive the molecular

constants since we are certain that no significant perturbations occur in
these lines. These values are only accurate realtive to P(1), i.e.
$\pm.02$ cm^{-1} in absolute value. However, there is a good probability that the
absolute frequency of P(1) can be improved by at least an order of magni-
tude in the near future.

Determination of α_3

The B_v values for a linear triatomic molecule can be expressed by
the equation

$$B_v = B_e - \alpha_3(v+1/2) - \gamma_{33}(v+1/2)^2 + f_1(\alpha_2) + f_2(\alpha_1) \qquad (6)$$

Let us deal with the progression of bands 000-00X. It is easy to see that

$$\frac{B_0 - B_v}{v} = \alpha_3 + \gamma_{33}(v+1) \qquad (7)$$

We have plotted the available data for this progression in Figure 3.
The points for the 002 band and the 004 band are the results of interfero-
metric measurements and derived from band origin plots, i.e. $\nu_+(J)$. The
method of R. R. V. is only a pseudo-interferometric method in that the
major burden of the wave length measurement falls upon the ability of
the diffraction grating to locate the center of the lines. The inter-
ferometer merely furnishes closely spaced, very accurately known reference
wave lengths and provides some slight additional help by means of vertical
dispersion. The value plotted for the 004 band also agrees with that
obtained by Douglas and Sharma.[4] The double point plotted for the 003
band is due to measurements of Douglas and Sharma.[4] The upper point is
the one given by the B' value obtained by them. The lower point we have
obtained from a band origin plot made from the data given in the paper of
Douglas and Sharma. The points for the 005 and 006 bands were again

obtained from band origin plots of the data given by Douglas and Sharma, and are much less precise than the other points due to weakness of the bands and their location in the spectrum. It should be stated that the spread of the points for the 003 band is well within the error stated by Douglas and Sharma for their determination of B'. We obtain $a_3=0.01003_4$, $\gamma_{33}=0.00018_8$ expressed in cm^{-1} as the values of these constants.

It is now possible to critically review the situation with regard to the c determination made by Rank, Ruth and Vander Sluis.[2] The discrepancy between their results and the present result involves a systematic error which it was not possible to evaluate at the time the previous work was done. No phase shift is to be expected for the aluminum interferometer coatings. Dr. Vander Sluis (private communication) has reexamined the interferometer calibrations and demonstrated no phase shift exists.

It must be remembered that the R. R. V. measurements are grating measurements. Harrison[8] has recently pointed out that the best diffraction gratings are capable of measuring wave length to only 1 part in 10^6. It could be presumed that the "Tuxedo" grating is at least as good and probably better than those used by Harrison.[8] If we assume wave length determination accurate to 5 parts in 10^7 for the "Tuxedo" grating in measuring the band lines which vary in intensity by a factor of 6, this would introduce a systematic error of ± 14 km per second. The error pointed out by Harrison[8] shows the futility of using grating measurements to obtain highly precise c measurements from data obtained in the photographic infrared.

However, it can be pointed out that this same grating effect of 5 parts in 10^7 would produce a systematic error in c of only ± 3 km

per second in a band measured at 4 microns.

The value for the velocity of light obtained by the band spectrum method as reported here is the same as the value obtained by other methods of measurement.[9]

We are indebted to Dr. W. F. Koehler of the Michelson Laboratory, Inyokern, for helpful discussion concerning the calculations of phase shift in multiple layer dielectric films. We express our thanks to Jean M. Bennett for help with the least squares calculations.

Table I.

$\nabla_+(J)-2\nu_0$	$2J^2$	L.M.S.C.	C-O	$\Delta_2 F'$	$4(J+1/2)$	L.M.S.C.	C-O
-6.0905	288	-6.0913	+.0008	72.8078	50	72.8082	+.0004
-8.2875	392	-8.2894	+.0019	84.4394	58	84.4393	-.0001
-10.8248	512	-10.8247	-.0001	96.0616	66	96.0624	+.0008
-13.6998	648	-13.6966	-.0032	107.6772	74	107.6763	-.0009
-20.4477	968	-20.4485	+.0008	113.4802	78	113.4795	-.0007
-22.3461	1058	-22.3461	.0000	125.0768	86	125.0775	+.0007
-24.3259	1152	-24.3273	+.0014	142.4522	98	142.4518	-.0004
-26.3932	1250	-26.3922	-.0010	154.0175	106	154.0178	+.0003

$B'-B''=-0.021161$, $D'-D''=7.66 \times 10^{-8}$ $B'=1.45707$ $D'=2.89 \times 10^{-6}$

Summary of data obtained in measurements of the 000-002 band of HCN. Frequency intervals measured, $\nabla_+(J)-2\nu_0$ and $\Delta_2 F'$ expressed in cm^{-1} in vacuo. Columns 3 and 7 headed L.M.S.C., least mean squares calculated values, cm^{-1} in vacuo. Columns headed C-O calculated minus observed values. The molecular constants are given in cm^{-1} in vacuo.

Table II.

Calculated frequencies in vacuum wave numbers of lines of the 002 band of HCN.

P(1)	6516.7043	R(11)	6551.8185
P(12)	6481.4117	R(12)	6554.2198
P(14)	6474.4539	R(13)	6556.5781
P(16)	6467.3315	R(14)	6558.8932
P(18)	6460.0453	R(15)	6561.1652
P(19)	6456.3410	R(16)	6563.3939
P(21)	6448.8106	R(17)	6565.5794
P(22)	6444.9846	R(18)	6567.7216
P(23)	6441.1184	R(19)	6569.8204
P(24)	6437.2119	R(21)	6573.8880
P(25)	6433.2653	R(22)	6575.8567
P(26)	6429.2787	R(23)	6577.7819
		R(24)	6579.6636
		R(26)	6583.2965

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4. A. E. Douglas and D. Sharma, J. Chem. Phys. 21, 448 (1953).

5. E. L. Yost, M.S. Thesis, The Pennsylvania State College, (1953).

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7. H. Barrell, J. Opt. Soc. Am. 41, 295 (1951).

8. G. R. Harrison, S. P. Davis and H. J. Robertson, J. Opt. Soc. Am. 43, 853 (1953).

9. J. W. M. DuMond and E. R. Cohen, Rev. Mod. Phys. 25, 691 (1953).

(14)

Legends for Figures

Figure 1. Plot of the ratio t_1/t_2 versus wave length λ as measured for 13.20 and 5.95 mm spacers of the Fabry Perot etalon.

Figure 2. Theoretically and experimentally determined phase shift in orders of interference versus wave length for triple coated dielectric interferometer plates.

Figure 3. $(B_0-B_v)/v$ versus $(v+1)$ for the progression $000-00X$ of HCN.
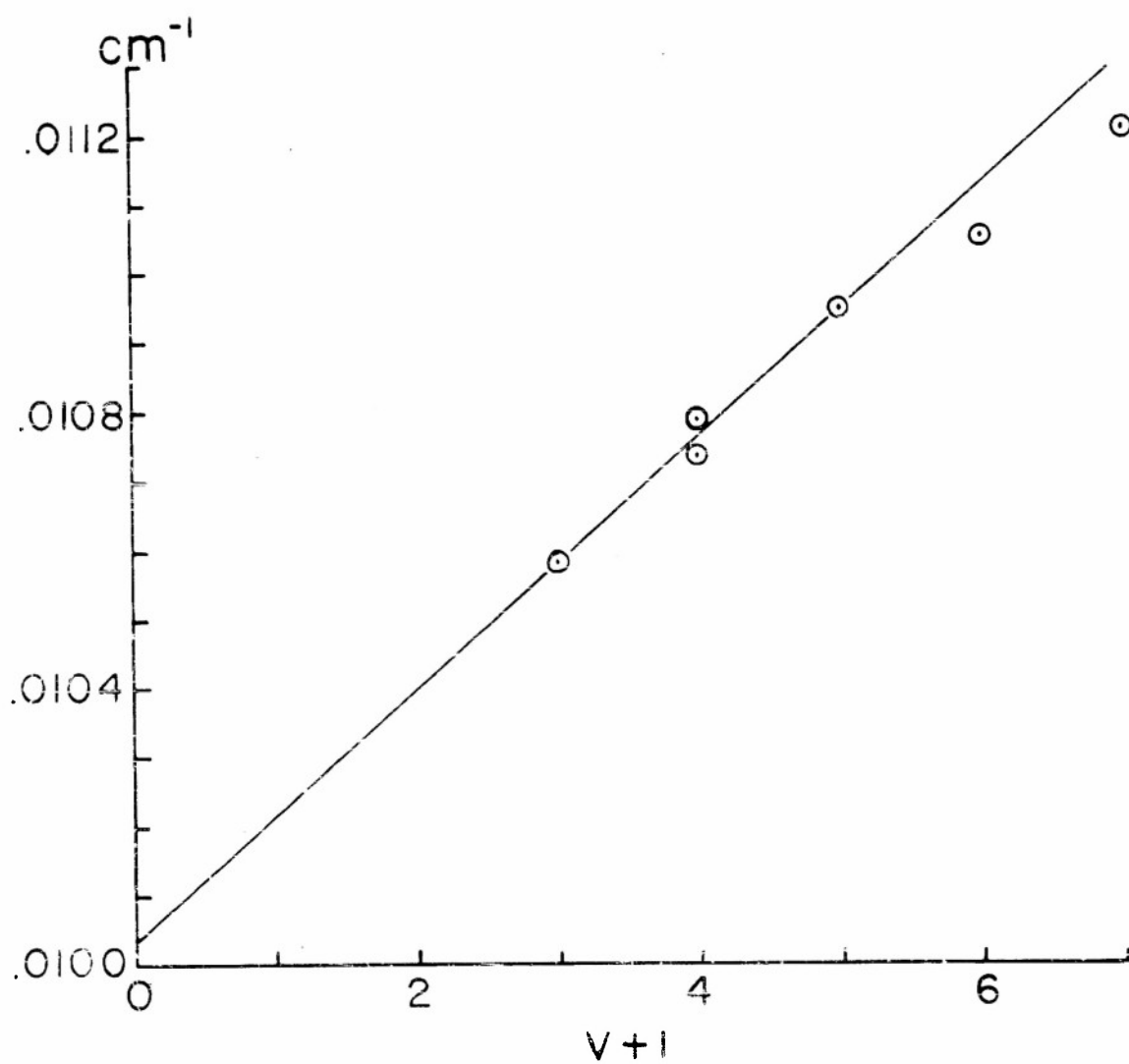
FIG. 1

WAVELENGTH IN MICRONS

FIG. 2

PHASE SHIFT
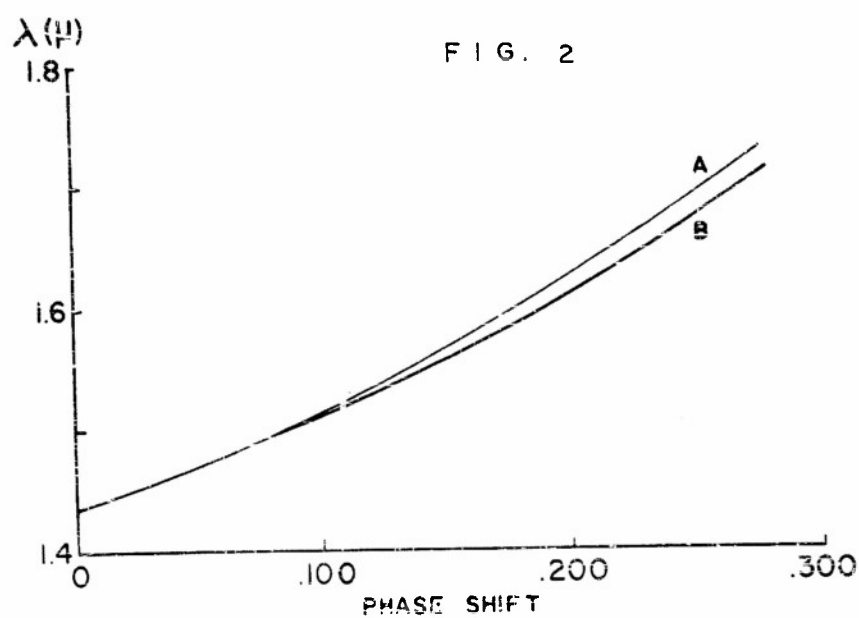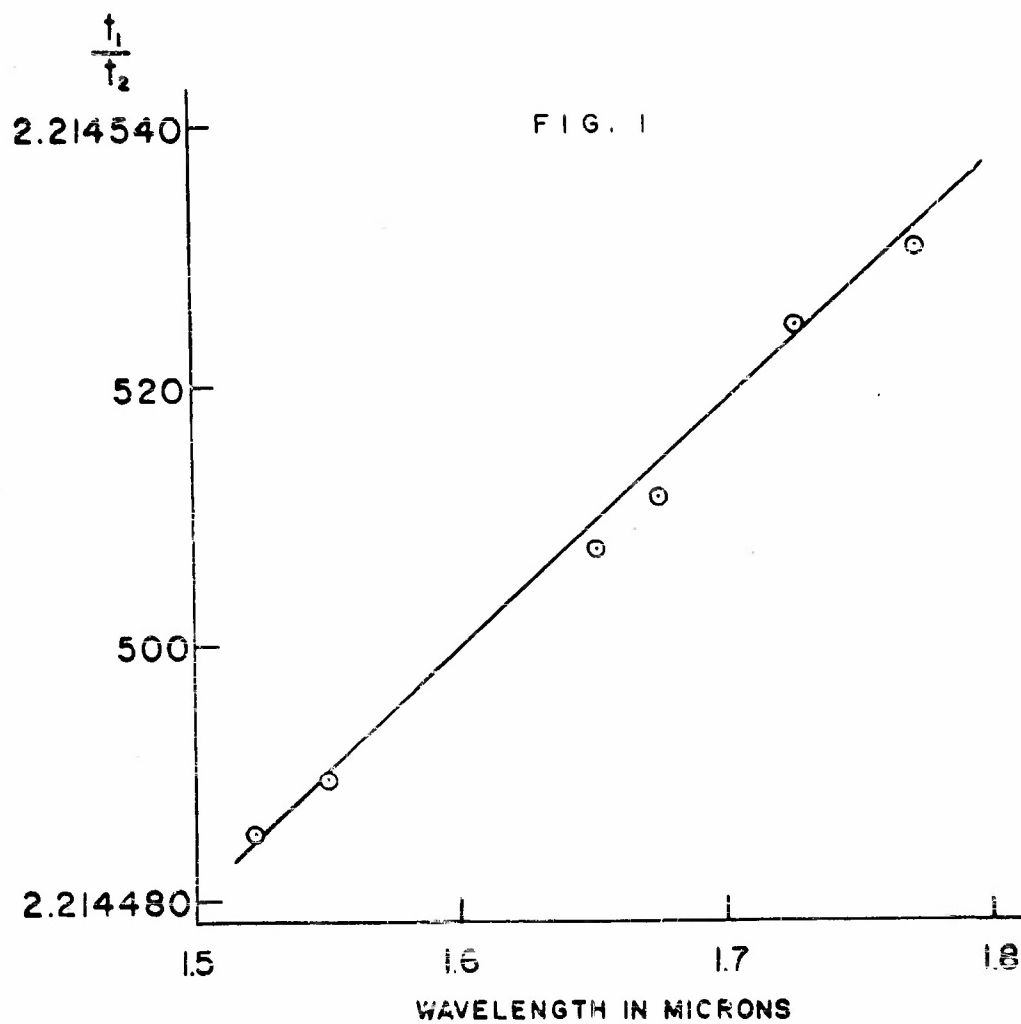
F I G . 3

AND RAMAN SPECTRA OF 1,1-DIMETHYLHYDRAZINE AND TRIMETHYLHYDRAZINE

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Infrared spectra of 1,1-dimethylhydrazine between 700 and 1600cm^{-1}

for the gas phase and between 700 and 3500cm^{-1} for the liquid phase and of

trimethylhydrazine between 700 and 3500 cm^{-1} for the gas and liquid phases

are reported along with the Raman spectra of the two compounds. Frequency

assignments are given for both compounds.

I INTRODUCTION

The fundamental frequencies of 1,1-dimethylhydrazine and trimethylhydrazine were

needed for calculations of the entropy of their vapors followed by comparison with the

calorimetric values to yield values of the barriers hindering internal rotation about

the N-N bond in the two compounds. Such a comparison has already been made for

hydrazine[4], methylhydrazine[5] and 1,2-dimethylhydrazine[6].

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[4]D. W. Scott, J. D. Oliver, M. E. Gross, W. N. Hubbard and H. M. Huffman, J. Am. Chem.
Soc., 71, 2293 (1949).

[5]J. G. Aston, H. L. Fink, G. J. Janz and K. E. Russell, J. Am. Chem. Soc., 73, 1939
(1951).

[6]J. G. Aston, J. G. Janz and K. E. Russell, J. Am. Chem. Soc., 73, 1943 (1951).

II EXPERIMENTAL

(a) <u>Materials</u>. - In both cases part of the calorimetric samples were used. The 1,1-dimethylhydrazine had 0.01 mole per cent impurity[7], and the trimethylhydrazine had

[7] J. G. Aston, J. L. Wood and T. P. Zolki, J. Am. Chem. Soc., 76, 0000 (1954).

2.1 mole per cent impurity[8]. The high percentage impurity in the latter case was due

[8] J. G. Aston and T. P. Zolki. To be published.

to the difficulty of preparation and a very closely boiling impurity which was difficult to remove by fractional melting with the quantity of sample at our disposal.

(b) <u>Raman Spectra</u>. - The Raman spectra were obtained with a three-prism spectrograph[9].

[9] D. H. Rank, R. Scott, and M. R. Fenske, Ind. Eng. Chem., Anal. Ed. 14, 816 (1942).

Excitation was the mercury blue line, 4358A, produced by a pair of low pressure mercury arcs[10] using a filter consisting of saturated aqueous sodium nitrite solution in two

[10] D. H. Rank and J. S. McCartney, J. Opt. Soc. Am. 38, 279 (1948); D. H. Rank, N. Sheppard, and G. J. Szasz, J. Chem. Phys. 16, 698 (1948).

cylindrical condensers. Eastman 103a-O spectroscopic plates backed with opaque red were used. The Raman shifts were determined from measurements on comparison spectra made using an iron-chromium (stainless steel) arc with a 20" f/8 camera (giving a linear dispersion of 19A/mm. at 4600A.) for the 1,1-dimethylhydrazine and with a 10" f/3.5 camera[11] (dispersion 32A/mm. at 4600A) for the trimethylhydrazine. Qualitative

[11] D. H. Rank, J. Opt. Soc. Am. 40, 462 (1950).

depolarization determinations were obtained photographically by the method of polarized incident light[12] using a 5" f/2 camera[11]. Exposure time up to 40 hr. were used.

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[12]A. E. Douglas and D. H. Rank, J. Opt. Soc. Am. 38, 281 (1948); D. H. Rank, B. D. Saksena, and E. R. Shull, Disc. Faraday Soc. No. 9, 187 (1950).

(c) Infrared Spectra. - The infrared spectra of the liquid and gas phases of the two compounds were obtained with a Perkin-Elmer Model 120 infrared spectrometer which had been modified to the Walsh double-pass optical arrangement[13] and equipped with

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[13]A. Walsh, J. Opt. Soc. Am. 42, 96 (1952).

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prisms of lithium fluoride, sodium chloride, and potassium bromide. The gas phase spectra were obtained with a 10 cm. cell at two pressures, a lower pressure to obtain detail in the strong bands and a higher one to detect weaker bands. The data on the two compounds are recorded in Tables I and II.

III DISCUSSION

In considering the spectrum of 1,1-dimethylhydrazine comparison was made with the assignment for trimethylamine[14] when assigning frequencies to the skeletal modes. This is

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[14]J. G. Aston, M. L. Sagenkahn. G. J. Szasz, G. W. Moessen and H. F. Zuhr, J. Am. Chem. Soc., 66, 1171 (1944).

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justified by the fact that the present molecule has an approximate geometrical symmetry of C_{3v} and the N-N force constant is not greatly different to that of C-C as can be seen by comparing the spectrum of methyl hydrazine[15] with that of dimethyl amine.

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[15]D. W. E. Axford, G. J. Janz, and K. E. Russell, J. Chem. Phys. 19, 704 (1951).

Regard was paid to this approximate symmetry in making use of the polarizations as a guide in the assignments. In assigning the NH stretching and bending frequencies comparison was made with the spectrum of methylhydrazine[15].

In assigning frequencies to the skeletal modes of trimethylhydrazine comparison was made with iso-pentane[16] and when treating the NH stretching and bending comparison

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[16]S. C. Schumann, J. G. Aston and Malcolm Sagenkahn, J. Am. Chem. Soc. 64, 1039 (1942)

---

was made with sym. dimethylhydrazine[15].

The assignment is given in Table III while Table IV gives the explanation of frequencies unassigned for 1,1-dimethylhydrazine as combinations of assigned frequencies. In the case of trimethylhydrazine there are six unassigned combination bands between 2458 and 2685cm^{-1} in the liquid infrared which do not appear in the liquid Raman spectrum. No attempt is made to assign these bands.

TABLE I

INFRARED AND RAMAN SPECTRA   1,1-DIMETHYLHYDRAZINE

| Infrared | | | | | | Raman | | | |
| (Gas) | | | (Liquid) | | | (Liquid) | | | |
ν	I^a	Structure	ν	I^a	Structure	$\Delta\nu$	I^a	Pol.^{b}	Breadth
						282	(w)	(p)	Diffuse & broad
						418	(m)	(p)	Narrow
						445	(m)	(p)	Narrow with diffuse wing at longer λ
803	(vs)	pqr	793	s	Broad	809	vs	p	Narrow
904	(s)	pqr	848	?					
961	m	q	944	s	Broad	957	w	pp?	Diffuse
1016	vw		1009	s	Broad	1027	m	p	Narrow
1046	vs	pqr							
1090	m	q	1069	s	Broad	1061	w	pp	Diffuse but not too broad
1139	s	q?	1140	s	?	1150	s	p	Narrow
1153	Branch on 1139								
1214	m	pqr	1201	s	?	1212	m	dp?	Narrow
			1243	m	?	1248	m	pp	Diffuse but narrow
1301	m	pqr	1321	s	?	1325	vvw	dp?	Diffuse
						1405	m	dp	Narrow
1457	m	pqr		vs		1423	s	dp	Broad
1593	m	?	----			1599	w	pp	Diffuse
			2764	m		2774	?		Covered by Hg line
			2811	m-		2817	?	p?	Narrow blends into Hg line
			2844			2849	m-s	p	Narrow
						2881	w	p	Narrow
			2944	m		2950	s	p	Narrow
			2975	w		2988	m	dp	Diffuse
			3126	vw		3141	m	p	Narrow
			3298	w		3330	vw	dp?	Diffuse

^{a}vvw, vw, m, s, vs denote respectively: extremely weak, very weak, weak, medium, strong and very strong.

^{b}dp, pp, cp denote respectively: depolarized, partly polarized, and polarized.

TABLE II

INFRARED AND RAMAN SPECTRA OF TRIMETHYLHYDRAZINE

Infrared						Raman			
(Gas)			(Liquid)			(Liquid)			
ν	I^a	Structure	ν	I^a	Structure	ν	I^a	Pol.	Breadth
						307	(w)	dp	Diffuse
						414	m	dp	Narrow
						436	m	p	Narrow
						498	s	p	Narrow
712	vw		688	vw					
783	vs		739	vs	Broad	747	s	pp	Narrow
888	vs		883	vs	Broad	884	m	p	Diffuse
1007	vs	Broad	958	m	Sharp	965	m	dp	Narrow
?4	w		1005	m	Sharp	1013	m	dp?	Narrow
			1077	m	Sharp	1083	m	pp	Narrow
1134	s		1119	m	Sharp	1126	ms	p	Narrow
1168	m		1165	w					
1180?	m		1189	m	Sharp				
1270	m		1212	m	Sharp	1215	w	dp	Diffuse
						1398	m	dp	Narrow
1477	s		1485	s	Broad	1448	s	dp	Broad and diffuse
			2458						
			2485						
			2535						
			2571						
			2593						
			2685						
2858	s		2858	vs		2843	m?	dp	
2970	s		2970	vs		2987	vs	dp	Broad
??2	m					3032	s	dp?	Narrow
3092	m	Sharp	3194	m					
3405	m		3405	vw		ca. 3400	m	p	Narrow

[a] See notes at foot of Table I

Table III

ASSIGNMENTS FOR 1,1-DIMETHYLHYDRAZINE - TRIMETHYLHYDRAZINE

1,1-Dimethylhydrazine		Trimethylhydrazine	
Assignment	Frequency	Assignment	Frequency
Skeletal bend	418	Skeletal bend	307
" "	445 (2)	" "	414
Skeletal stretch	803	" "	436
" "	904	" "	498
" "	961	Skeletal stretch	712
Rocking	961	" "	783
"	1046 (2)	" "	888
"	1090 (2)	" "	1007
"	1139	CH_3 rock	1044 (2)
CH_3 bend	1301 (4)	" "	1134 (2)
" "	1405	" "	1168 (2)
" "	1457	NH bend	1180
NH_2 bend	1593	" "	1270
CH_3 stretch	2950 (3)	CH_3 bend	1398 (3)
" "	2988 (3)	" "	1477 (6)
NH_2 "	3741	CH_3 stretch	2858 (4)
" "	3330	" "	2970 (2)
		" "	3082
		" "	3092 (2)
		NH stretch	3405

Table IV

COMBINATION FREQUENCIES FOR 1,1-DIMETHYLHYDRAZINE

Infrared (gas)	Raman (Liquid)	Combination
1214	1212	418 + 803
	2774	418 + 803 + 1593
	2817	1405 + 1423
	2849	2 x 1457
	2881	1593 + 1301

INDEX OF REFRACTION OF AIR IN THE INFRARED [*]

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A new formula has been derived by Edlen[1] for the dispersion of air throughout the entire spectrum. This formula was derived making use of only data obtained in the visible and ultra violet. The only measurements available for the index of refraction of air beyond 1.0μ are those reported recently by this laboratory.[2] We have improved our measurement technique in that greatly improved thermal stability of the etalon has been achieved. We have constructed all the metal parts of the etalon of invar and the plates of fused quartz.

New measurements have been made of the index of refraction of air making use of the method of exact orders. A 13.2 mm spacer was used for the plate separation. We have checked our method by determining the index of refraction in the visible where precise measurements are available. In the visible use was made of the Hg green line which can be reversed when sufficiently high pressure is used in the arc. The yellow Hg line was used as the emission base for one of the I_2 absorption lines. We have also made index of refraction determinations by a method which made use of emission lines from a Hg198 lamp. Measurements by this method were made at λ_v = 15300A and λ_v = 5462.3A. A 29 mm spacer was used in the inter- ferometer for the measurements made with the emission lines.

The results of our new measurements are summarized in Table 1. Our measurements are not of sufficient precision to compete with the best index measurements made in the visible part of the spectrum. The measure-

ments in the visible were made only to serve as a check on the reliability of our methods, since our methods seem to have the same sensitivity in the infrared as in the visible part of the spectrum. Within the limits of our error we obtain the index of refraction of air predicted by the Edlen[1] formula for the visible part of the spectrum.

In the infrared our measurements of $(\mu-1)_s \times 10^6$ are greater than that predicted by the Edlen formula by 0.43. Our result is in accord with the measurements of Essen[3] for 3 cm waves which yields $(\mu-1)_s \times 10^6 = 273.05$. Dr. Essen (private communication) informs us that this value should be reduced to 272.85 to bring the measurements into accord with optical measurements. The correction is due to the effect of one of the microwave oxygen absorption lines. The value calculated for $(\mu-1)_s \times 10^6$ for 3 cm waves from the Edlen formula is 272.55 which makes the measured value high by 0.30 with reference to the Edlen formula. Thus, the weight of the experimental evidence seems to show that the Edlen formula predicts a $(\mu-1)_s$ too small by slightly more than one part in 1000 in the infrared region of the spectrum beyond 1 micron.

Our experience with the Fabry Perot etalon in making the index of refraction measurements of air leads us to the conclusion that much more precise measurements can be made with a modified Twyman Green interferometer where lower fringe sensitivity must be accepted but very long air paths can be used. The thermal disturbance created in the interferometer by evacuating the cell or filling with gas would be negligible in the Twyman Green while in the Fabry Perot this thermal effect is large and hard to completely eliminate.

References

1. B. Edlen, J. Opt. Soc. Am. <u>43</u>, 339 (1953).

2. D. H. Rank, E. R. Shull, Jean M. Bennett and T. A. Wiggins, J. Opt. Soc. Am. <u>43</u>, 952 (1953).

3. L. Essen, Proc. Phys. Soc. (London) B 66, 189 (1953).

- 4 -

λ_v A.	Source	$(\mu-1)_s \times 10^6$ Meas.	$(\mu-1)_s \times 10^6$ Calc.Edlen	No. Det.	A.D.M. $\times 10^6$	M - C $\times 10^6$
5462.3	Hg R	277.93	277.86	5	.04	+.07
5462.3	Hg198E	277.90	277.86	2	.25	+.04
5792.3	Hg R	277.22	277.26	5	.11	-.04
15300	Hg198E	273.67	273.21	3	.06	+.46
15349	P(1)HCN	273.81	273.21	4	.14	+.60
16541	R(3)CH$_4$	273.43	273.12	5	.09	+.31

Average M - C Infrared + .43 x 10^6

Table 1. Summary of index of refraction of air measurements. λ_v refers
to wavelength in vacuo. Column headed source refers to source of spectrum
line used. Sources, e.g. Hg198E, means the measurements were made by an
emission technique. All other measurements made making use of absorption
lines. Column 5 gives the number of determinations made. Column 6, A.D.N.,
average deviation from the mean; column 7 measured minus calculated values
of $(\mu-1)_s$. All index of refraction measurements are based on dry CO_2-free
air.

A SIMULATED CHANNEL SPECTRUM[*]

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Abstract

In order to obtain the highest accuracy in interferometric wavelength measurements with energy integrating devices, the theory of the Fabry Perot interferometer must be extended. In this paper the portion of the theory dealing with the integrated energy in the part of the Fabry Perot ring system virtually intercepted by a slit of finite length is presented. We are assuming that the interferometer is placed in parallel light and an infinitely narrow band of wavelengths is used. For this situation, it is shown how the order at the center of the ring pattern corresponding to maximum and minimum energies respectively varies with slit height. The contrast is then determined as a function of slit height. The experimental methods for measuring these quantities are described and the results compared with theory. The theory is also extended to the case of an actual channel spectrum where a finite band of wavelengths is present.

A Fabry Perot etalon used in conjunction with a high resolution grating spectrograph is capable of producing a sensitivity of wavelength measurement in excess of 1 part in twenty million in the 1 to 2 micron region of the infrared spectrum.[1] The conversion of this high wavelength sensitivity into relative and absolute wavelength measurement demands careful scrutiny of the theory of the etalon. In this paper we shall treat only the portion of the theory dealing with the integration of the energy in the part of the ring system virtually intercepted by a slit of finite length. The problem of phase shift in the interferometer films as a function of wavelength, particularly for multi-layer dielectric films, will be treated in a subsequent paper. In addition, we shall limit our treatment to the case of parallel light since for the most precise measurements the slight extra effort necessary to use parallel light is fully justified because of the simplification of the theory involved.

A theoretical attempt to solve the problem treated in this paper has been made by Jaffe[2] both for parallel and convergent light. Jaffe's treatment, however, involves an approximation in his original integral so that his conclusions are not strictly valid. When his theory is applied to wavelength measurements, the predicted shifts in the maxima of the fringes do not actually occur. In addition, the visibility curves obtained from this treatment are incorrect.

Theoretical treatment

Referring to Fig. 1 and making use of the well known expression for the distribution of light in a Fabry Perot interference pattern, the light intensity at any angle θ on the detector arising from any point on the uniformly illuminated exit slit is given by (in the absence of absorption):

$$I = I_o \frac{1}{1 + F \sin^2\left(\frac{2\pi t}{\lambda}\cos\theta\right)} \tag{1}$$

where I_o is the intensity of the light incident on the etalon which can
be set equal to unity, $F = \frac{4R}{(1-R)^2}$ where R is the reflectivity of the
interferometer plates, t the separation of the plates and λ the wavelength
of light in the interferometer. The total light flux S_λ intercepted by
the detector is:

$$S_\lambda = W \int_{-Y}^{+Y} I_\theta \, dy \tag{2}$$

where W is the width of the exit slit which is assumed to be very small.
Making elementary substitutions we can write Eq. 2 as:

$$S_\lambda = 2WL \int_0^{\Phi} I_\theta \, d\theta + 2WL \int_0^{\Phi} I_\theta \tan^2\theta \, d\theta \tag{3}$$

Since the maximum value of $\Phi \sim 0.01$ radian, the magnitude of the second
integral in Eq. 3 is approximately 10^{-4} that of the first integral and
hence can be completely neglected.

Let us call the phase difference between successive interferring
beams at the center of the pattern $\delta_o = \frac{4\pi t}{\lambda}$ and $\delta = \delta_o \cos\theta$. We then
obtain from Eq. 3:

$$S_\lambda = -\frac{2WL}{\delta_o} \int_{\delta_o}^{\delta_o - \epsilon_s} \frac{1}{(1 - \delta^2/\delta_o^2)^{1/2}} \cdot \frac{1}{1 + F \sin^2 \delta/2} \, d\delta \tag{4}$$

where $\epsilon_s = \frac{\delta_o}{2}\phi^2$, $\cos\theta = 1-\frac{\theta^2}{2}$ and $\sin\theta = (1-\delta^2/\delta_o^2)^{\frac{1}{2}}$ Eq. 4 can be

expanded into a series and the integration performed. The series, however,

converges so slowly that this analytic solution of the problem is not

useful.

We have solved our problem for a specific case by numerical integration

of Eq. 1. This process, while somewhat tedious, gives us the desired

information. By plotting the function I_θ versus θ for progressively

changing orders of interference n_o at the center of the ring pattern, $n_o = \frac{\delta_o}{2\pi}$,

and then numerically integrating the area under these curves, one can

obtain the energy integral S_λ as a function of the number of rings Δ

intercepted by the detector ($\Delta = \epsilon_s/2\pi$) . From this data one can then

determine which values of n_o give maximum and minimum values respectively

for S_λ for a given Δ, and also the ratios $K = \frac{S_\lambda \ max}{S_\lambda \ min}$ for each case.

In order to perform our numerical integration, it is necessary to

know the reflectivity of the interferometer plates and the separation of

the plates as well as the wavelength of light used. Our particular

interferometer plates were coated with $\lambda/4$ films of ZnS - MgF$_2$ - ZnS

and had a directly measured reflectivity of 62.2% for λ 5770 A. We have

obtained the reflectivity which we have used in our calculations in a

somewhat different manner than direct measurement for a number of reasons.

We have chosen $K_o \approx \lim_{\Delta\to 0}\frac{S_\lambda \ max}{S_\lambda \ min}$ as the definition of the "Fabry Perot

reflectivity" of our etalon plates. K_o was obtained by measuring the

contrast K for very small exit slit heights (see Fig. 2) and then

extrapolating to zero slit height. The value obtained for R by this

method of 57.2%.

The process of using the reflectivity derived from K_o seems justified in that the value of R calculated from these measurements should be the effective reflectivity R_e responsible for the intensity detail in the multiple beam interference pattern. The physical reasons for R_e being slightly smaller than the directly measured R are at least threefold. First, the two plates have slightly different reflectivities since they were prepared separately; second, there is a slightly imperfect figure on the interferometer plates; and third, not strictly monochromatic light was used in making the contrast measurement. The third reason probably had only small effect since the breadth of the Hg 198 lines only becomes grossly observable when t = 25 mm or greater. Our contrast measurements were made with t = 6 mm.

Experimental measurements

It is not possible to make accurate measurements of the relationship between the number of rings Δ intercepted by the detector and the fractional order ε at the center of the ring pattern by using a channel spectrum. This is due to the finite resolving power of the spectrograph which prevents the light fed into the interferometer by the monochromator from being strictly monochromatic. Fortunately, it is possible to strictly simulate the channel spectrum using monochromatic light. An interferometer ordinarily produces a channel spectrum if the wavelength is modulated at the exit slit. However, the simulation of a channel spectrum using monochromatic light can be accomplished by modulating the wavelength in the interferometer by changing the air pressure.

A schematic diagram of our apparatus is shown in Fig. 2. S_1 is the exit slit of the grating monochromator. The slit is provided with a draw slide which allows the length of the slit to be varied at will, thus permitting the formation of the desired number of interference rings. L_1 and L_2 are the collimating and objective lenses respectively, and P is a multiplier phototube whose output is amplified and recorded on a Brown recorder. The position of the Fabry Perot etalon E mounted in a chamber so that the air pressure can be varied at will is shown in Fig. 2. It should be noted that E is placed at the exit pupil of the equivalent telescope, the objective of which is the mirror $M_1{}^1$ focussing light from the grating, and the eyepiece is the collimator L_1 for the interferometer in Fig. 2. At the position E, the area of the parallel beam is a minimum since all parallel rays must pass through this position where the image of the entrance pupil is formed. B indicates the position of a plane parallel plate which is used as a beam splitter to facilitate observations. D is a Dove or so-called vertical rotating prism whose function is to rotate the image of the slit through 90°, i.e. from a vertical to a horizontal position. The angular diameter of the bright rings can thus be measured directly by means of the spectrometer indicated in the figure by its telescope T. The spectrometer was capable of measuring angles to 10^M of arc.

Light from a Hg 198 lamp furnished by the National Bureau of Standards was used for all measurements. The exit slit S_1 illuminated by one of the mercury lines was diaphragmed to the desired length by means of the draw slide. The air pressure was modulated by pumping or allowing air to leak slowly into the etalon. As the modulation of wavelength progressed, the recorder indicated the energy present in the interference pattern. The

maxima and minima could be precisely ascertained from the recorder chart.
Our procedure was to find a maximum or minimum by changing the air pressure.
When such a maximum or minimum was produced, the modulation was discontinued
and the angular diameter of the rings measured by means of the spectrometer
T. To observe the rings, it was only necessary to open the draw slide
regardless of the slit height used for setting on maxima or minima. The
fractional order of interference ε at the center of the pattern can be
calculated from the well-known relationship $\varepsilon + p = \frac{2t}{\lambda} \phi^2$, where ϕ is the
angular diameter of the interference ring and p the number of bright rings
counting from the center of the pattern. The ring diameters could be
measured with sufficient precision so that ε could be determined to somewhat
better than 0.01 orders.

The curve A shown in Fig. 3 gives the results of our measurements of
order ε at the center of the pattern plotted against the number of rings Δ
subtended by the slit when the intensity is a maximum. Curve B is the
result of the numerical integration described in the theoretical section
of this paper. Curve A, Fig. 4, represents the experimental result obtained
when the intensity produced is a minimum, while curve B is again the
calculated result. Fig. 5, curve A, is a plot of the measured value of
the contrast $K = \frac{S_{\lambda\ max}}{S_{\lambda\ min}}$ versus the number of rings Δ subtended by the slit.
Curve B, Fig. 5, is the calculated contrast curve again obtained from the
numerical integration process. Fig. 6 is an enlargement of part of the
curves shown in Fig. 5.

The results given in Figures 3,4,5 and 6 show that the agreement
between theory and experiment is excellent. The minor differences between
calculated and observed curves are near the limit of experimental precision
obtainable with the present apparatus. The relatively larger discrepancies

between curves A and B in Fig. 4 are due to two main factors: first, the
intensity minima are much broader than the maxima and hence the error made
in modulating the air pressure is roughly 3 or 4 times that made in setting
on a maximum. Second, since ε shifts much more rapidly with Δ for a
minimum, stricter requirements are set on the measurement of the exit slit
height. In our experiment, a cathetometer was used to measure the slit
height and settings were made to better than 0.1 mm. For a slit height
corresponding to one ring, this would introduce an error in Δ of 0.05%.

It should be noted that the maxima and minima of the integrated energy
are exactly 0.5 orders apart only when the angular subtense of the slit
approaches zero. The order shifts slowly for maxima as a function of
angular subtense, while the minima are displaced very much more. Fig. 7
reproduces some of the fringes obtained by using monochromatic light and
slowly changing the air pressure in the interferometer, as previously
described. Curves A B and C show these simulated channel fringes produced
with exit slit heights corresponding to 2.87, 0.99 and 0.13 rings respec-
tively. It will be noted in Fig. 7, curve A that while the shape of the
fringes is somewhat determined by the rate of pumping, the asymmetry is
real, and shows up in the same way both when air is let into and out of
the etalon. Also note that the fringe corresponding to Δ = 0.13 ring
is completely symmetric.

Asymmetry of the channel fringes can easily be eliminated by arranging
the apparatus so that only a small fraction of a ring is subtended by the
exit slit. Under this condition, the contrast is also improved and any
fringe shift of maxima with wavelength is minimized and can be corrected for
if necessary.

Application of Theory to the Channel Spectrum

As was noted previously in this paper, the theory developed is not directly applicable to an actual channel spectrum. In order to mathematically approximate the real situation in which a narrow band of wavelengths is fed into the interferometer by the grating monochromator, the narrow band was replaced by several discrete wavelengths such that the difference between extremal lines equalled the band width to be approximated. Then the distribution of light in a Fabry Perot interference pattern for this system was obtained by calculating I_θ from Eq. 1 for each wavelength and then averaging all the values for a given θ. When the resulting pattern was compared to the pattern for central wavelength alone, it was seen to have much lower maxima corresponding to the bright rings and more light in the minima. If the band to be approximated was sufficiently narrow, the resulting interference pattern was almost that obtained with monochromatic light and interferometer plates of a lower reflectivity. However, for wider band widths, the intensity pattern could not be approximated in this manner.

As an example, intensity curves were computed for five wavelengths spreading 0.176 A around a central component λ 17,670 A (choosing an interferometer spacing such that the order of interference at the center of the pattern was 14,930.00). The reflectivity of the plates was assumed to be 69%. The resulting curve with the maxima normalized to unity is the solid curve shown in Fig. 8. When the apparent reflectivity for this curve was computed from the relation $\frac{I_{min}}{I_{max}} = \frac{(1-R)^2}{(1+R)^2}$, it was found to be 62.4%. The curve for monochromatic light λ 17,670 A and this lower reflectivity was then computed and is the dotted curve in Fig. 8. A more

detailed account of these calculations is given in the master's thesis of Pisaniello.[3]

It is seen from the curves that one makes an appreciable error by using the approximation of monochromatic light and a lower reflectivity. The percent difference between the areas under the two curves is 11.2% for $\Delta = 0.1$ ring and this difference increases with increasing Δ, giving an error of 17.1% for $\Delta = 3.5$ rings. A slightly closer approximation of the average curve might have been made by assuming monochromatic light and a reflectivity lower than 62.4%. However, if one wished to obtain a contrast curve for a channel spectrum similar to Fig. 5, it would be best to start with the $I_{\theta \text{ Average}}$ curves using enough wavelengths to approximate the continuum to the desired accuracy, and then proceed as outlined in the theory section of this paper. This was not done in our case since it was felt that the knowledge obtained did not justify the extremely large amount of labor involved. However, one of the large automatic computors could easily solve this sort of problem.

1. D. H. Rank, E. R. Shull, Jean M. Bennett, and T. A. Wiggins, J. Opt. Soc. Am. 43, 952 (1953).

2. J. H. Jaffe, J. Opt. Soc. Am. 43, 1170 (1953).

3. P. J. Pisaniello, M.S. Thesis, The Pennsylvania State University, 1954 (unpublished).

Legends for Figures

Figure 1: Interferometer placed in parallel light. S_1 source, L_1 collimating lens, E Fabry Perot etalon, L_2 objective lens of focal length L, S_2 detector.

Figure 2: Diagram of apparatus. S_1 exit slit of grating monochromator, L_1 and L_2 collimating and objective lenses respectively, P multiplier phototube, E Fabry Perot etalon, B beam splitter, D Dove or vertical rotating prism, T telescope of spectrometer.

Figure 3: Curves A and B show the experimental and calculated order ε at the center of the ring pattern plotted against the number of rings Δ subtended by the slit when the intensity is a maximum.

Figure 4: Curves A and B show the experimental and calculated orders ε plotted versus Δ when the intensity is a minimum.

Figure 5: Plot of the measured and calculated values of the contrast $K = \dfrac{S_{\lambda\,max}}{S_{\lambda\,min}}$ versus the number of rings Δ subtended by the slit.

Figure 6: Enlargement of part of Fig. 5.

Figure 7: Parts A, B and C show fringes of the simulated channel spectrum produced when the slit subtended 2.87, 0.99 and 0.13 rings respectively. Part A shows fringes produced by modulating the air pressure in opposite directions.

Figure 8: Intensity distributions I_θ versus θ for (A) monochromatic light, and (B) a narrow band of wavelengths. For curve A, $\lambda = 17,670$ A, $n_0 = 14,930.00$ and R = 62.4%. Curve B is an average of five wavelengths centering around $\lambda = 17,670$ A with 0.176 A between extremal lines and R = 69%.

FIG. 2

FIG. 4

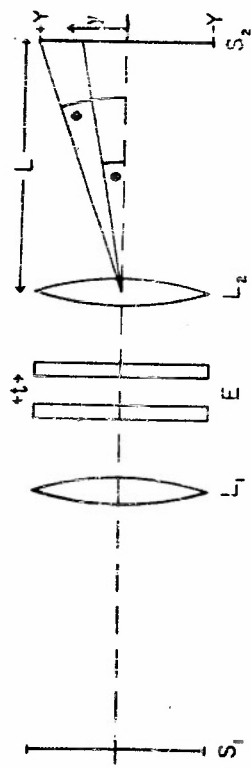FIG. 1
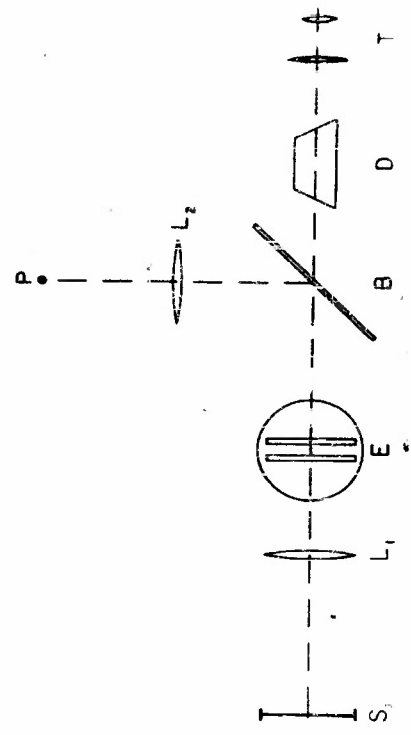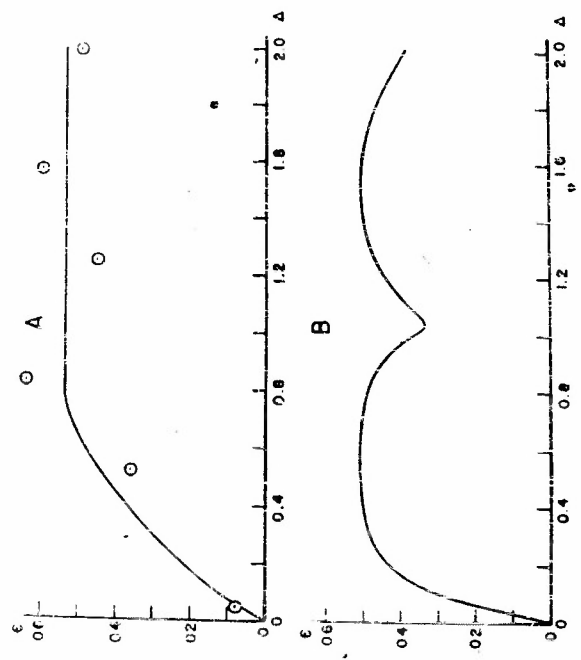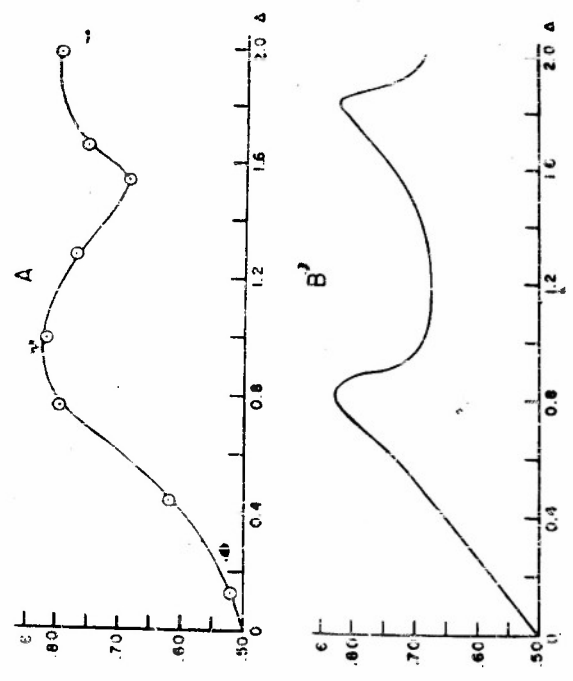
FIG. 3
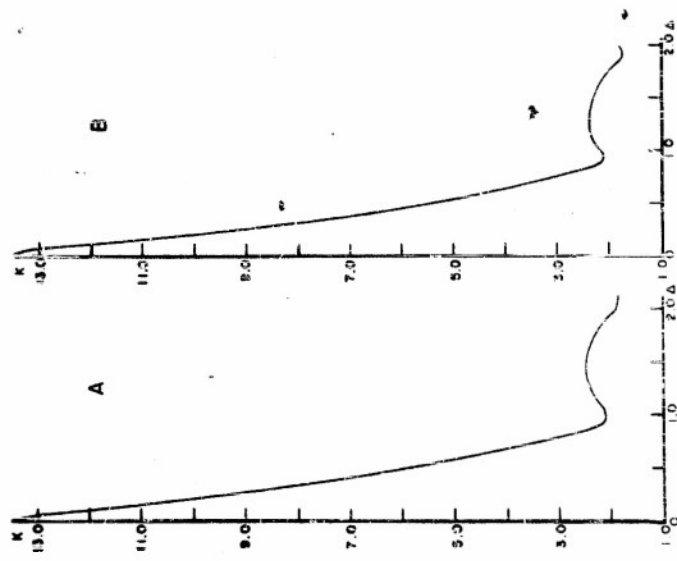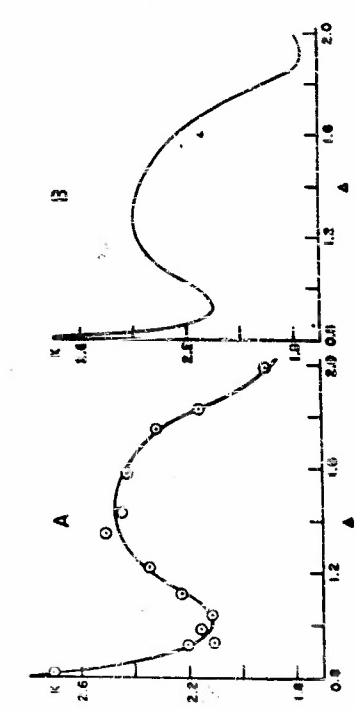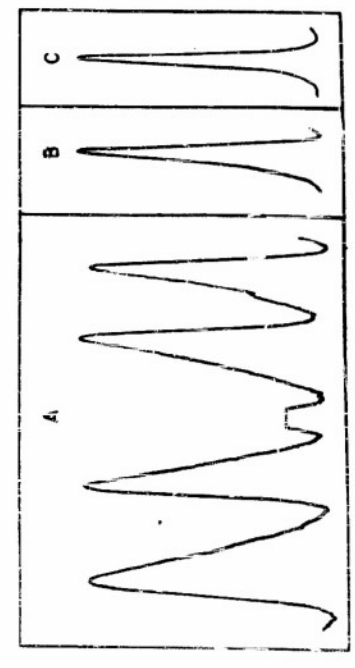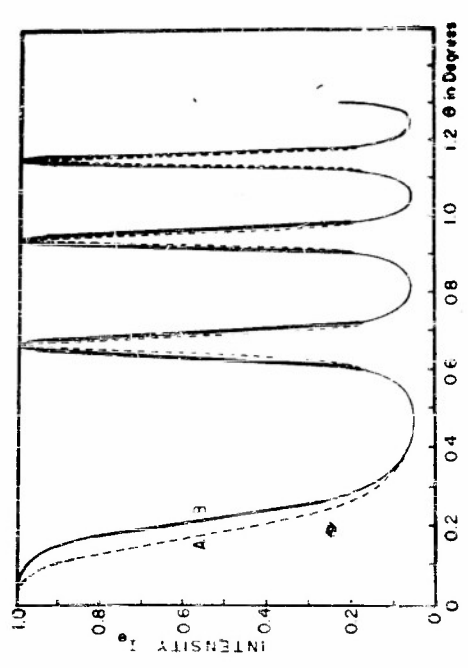
FIG. 8

FIG. 7

FIG. 5

FIG. 6

THE PROBLEM OF PHASE VARIATION WITH WAVELENGTH IN DIELECTRIC FILMS. EXTENSION OF INTERFEROMETRIC STANDARDS INTO THE INFRARED.*

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Abstract

A purely interferometric method is suggested by which known stan-
dard wavelengths in the visible part of the spectrum are used to
determine new wavelength standards in the infrared. The application of
the method of exact fractions to measurements made using a Fabry Perot
interferometer whose plates are coated with highly reflecting dielectric
films is discussed. It is shown that the large phase corrections
introduced by these films may be reduced to differential corrections
if relative wavelength measurements are made near wavelengths for which
the phase change on reflection is π. A method of experimentally deter-
mining both the differential correction and wavelengths at which the
phase change of π occurs is suggested.

-2-

It is well known that the most difficult problem with regard to measurement of precise absolute or relative wavelengths is the determination of the phase variation with wavelength produced by the interferometer films. Meissner[1] has given a rather complete treatment of the mechanics of evaluating these phase changes, which is applicable when the phase correction is small.

Absorption of metal films makes them undesirable for interferometer plate coatings for the infrared region of the spectrum. Multi-layer dielectric films can be produced which have negligible absorption and have the desired reflectivity. Interferometers coated with these dielectric films can be used in conjunction with high resolution grating spectrographs to produce sensitivity of wavelength measurement comparable to the best obtainable in the visible region of the spectrum.[2]

The absence of absolute interferometric wavelength standards in the infrared is a very serious obstacle to the production of accurate relative wavelength measurements which are necessary for the precise determination of molecular constants.

In this paper we shall explore the possibility of making interferometric comparison measurements between "known" lines in the visible part of the spectrum and lines in the near infrared. Our experience has shown that the evaluation of the phase change on reflection vs. wavelength characteristics of the multi-layer dielectric films with the requisite precision is formidable. The magnitudes of these phase changes are much larger than those produced by silver. It seems impractical to attempt to transfer interferometric wavelength measurements

from the photographic region to the 1.5 to 2.5 μ region in a step-wise
fashion because of the cumulative error which would be introduced in
determining the phase correction over the necessarily large wavelength
interval. In view of the above-mentioned difficulty, we shall attempt
to show that the direct determination of the phase change vs. wavelength
function can be made unnecessary, and that it should only be necessary
to measure certain film constants and phase change vs. wavelength
differentials at the proper wavelengths.

Theory of the Interferometer:

We shall consider briefly the fundamental equations for construc-
tive interference for a Fabry Perot etalon in which we have a phase
shift $\varphi = \pi + \delta$ resulting from reflection at an interferometer plate.
For normal incidence the equation is:

$$N \lambda = 2\left(n t^* + \frac{\lambda}{2} + \frac{\lambda \delta}{2\pi}\right) \qquad (1)$$

where N is the actual order of interference, t^* the mechanical separa-
tion of the etalon plates, n the index of refraction of the medium in
which the plates are immersed, δ the departure of the phase angle from
π and λ the vacuum wavelength of the light. If we substitute
$\bar{N} = N-1$, we can write Eq. (1) in the form:

$$N^* \equiv \bar{N} - \frac{\delta}{\pi} = \frac{2 n t^*}{\lambda} \qquad (2)$$

It may be observed that the method of exact fractions can be applied
strictly to Eq. (2) since this equation is identical in form to the
equation for the etalon in which there is no phase shift. It is further

seen that the correction to the order resulting from the deviation in phase change from π is $\delta/2\pi$ per plate.

We shall develop the simple theory necessary for the experimental determination of the phase shifts in a more general form than in our previous paper.[2] This procedure is necessary in order to obtain the fine detail which can later be made use of to apply the phase shift results in a differential manner.

Let us consider two interferometer spacers of mechanical thickness $t_1{}^*$ and $t_2{}^*$, and two wavelengths λ_1 and λ_2. The orders of interference N at the centers of patterns are given, for normal incidence, by:

$$N_1 = \frac{2nt_1^* + d\epsilon_1}{\lambda} \equiv \frac{2nt_1}{\lambda_1}$$

$$N_2 = \frac{2nt_2^* + d\epsilon_1}{\lambda_1} \equiv \frac{2nt_2}{\lambda}$$

$$N_3 = \frac{2nt_1^* + d\epsilon_2}{\lambda_2} = \frac{2nt_1 + d\epsilon_2 - d\epsilon_1}{\lambda_2} = \frac{2nt_1 + d\epsilon}{\lambda_2} \tag{3}$$

$$N_4 = \frac{2nt_2^* + d\epsilon_2}{\lambda_2} = \frac{2nt_2 + d\epsilon_2 - d\epsilon_1}{\lambda_2} = \frac{2nt_2 + d\epsilon}{\lambda_2}$$

It is easy to see that $d\epsilon = d\epsilon_2 - d\epsilon_1 = \frac{\lambda_2 \varphi_2 - \lambda_1 \varphi_1}{\pi}$. The order change dN introduced by the phase shift is:

$$dN = \frac{d\epsilon}{\lambda_2} = 1 - \frac{\lambda_1}{\lambda_2} + \frac{1}{\pi}\left(\delta_2 - \delta_1 \frac{\lambda_1}{\lambda_2}\right)$$

$$= \frac{2nt_2^*(\beta_2 - \beta_1)}{\lambda_2(1 - \beta_2)} \tag{4}$$

where $\rho_1 = N_1/N_2$ and $\rho_2 = N_3/N_4$. It will be noted that the last expres-

sion of Eq. (4) is identical to the previous result[2] derived for d_6.

Measurements made with the interferometer deal with the optical thickness of the interferometer spacer. It must be pointed out, however, that in employing the method of exact fractions, the method itself by the use of the equation $N_i^* \lambda_i = 2nt^* = N_k^* \lambda_k = \ldots$ forces the determination of the mechanical spacer. This last-mentioned equation is the only one of its type which can be written so long as $\varphi \not\equiv 0$ regardless of whether φ varies with wavelength or not. Only if $\varphi \equiv 0$ for all wavelengths can N and t be used for N^* and t^* where nt is the optical thickness of the interferometer.

Once t^* has been determined, a knowledge of the phase shift at any wavelength λ will allow us to calculate λ if the corresponding N^* is known. We shall show in the next section of this paper that δ's can be calculated for dielectric films with sufficient precision so that the method of exact fractions will allow a unique choice of N^* for the different wavelengths. Once these values of N^* have been obtained, the mechanism of the set of equations (3) and (4) can be applied and accurately determined values of δ as a function of wavelength can be experimentally determined.

It is not necessary to use the most general expression (4), since a simple transformation can be made so that only the δ will enter the phase shift vs. wavelength function and thus allow the use of N^* directly instead of N as required by (4). Letting $\bar{\rho}_1 = \bar{N}_1/\bar{N}_2$ and $\bar{\rho}_2 = \bar{N}_3/\bar{N}_4$ it is easily seen that Eq. (4) reduces to :

$$d\overline{N} = \frac{1}{\pi}\left(\delta_2 - \delta_1 \frac{\lambda_1}{\lambda_2} \right) = \frac{2n\, t_2^*\,(\bar{\rho}_2 - \bar{\rho}_1)}{\lambda_2 (1 - \bar{\rho}_1)} \qquad (5)$$

The essential process practically used to obtain the barred quantities is as follows: the N^* quantities are obtained applying the method of exact fractions after preliminary phase correction to the observed fractional order of interference. After the integral orders for the various wavelengths have been chosen applying the method of exact fractions, $\bar{N}$ is obtained by using the integral N^* value and the measured fractional order, vide Eq. (2).

We can summarize the problem of determining the phase shift vs. wavelength in the following manner. First a calculation of δ_i is made from electromagnetic theory and corrections applied to the observed fractional orders of interference. The method of exact fractions is now applied, which, combined with the preliminary mechanical measurement of the spacer, yields N^* values for the different wavelengths and serves to give a second approximation to t^*, the mechanical length of the interferometer spacer. The measured fractional orders are now combined with the integers obtained from the method of exact fractions, thus giving us the $\bar{N}$ quantities which allow the use of Eq. (5). The application of Eq. (5) allows the phase shift vs. wavelength correction to be derived directly from the experimental measurements made with two different interferometer spacers. It must be pointed out that Eq. (5) is not capable of giving $\delta(\lambda)$ values absolutely, but only the quantitative measure of the change of δ with wavelength, which is all that is necessary to measure an unknown wavelength compared to a known wavelength.

Calculation of Phase Change on Reflection for Dielectric Films

Fortunately the small conductivity and freedom from significant absorption greatly simplifies the theoretical procedure for the calculation of phase shift and reflectivity of dielectric films making use of electromagnetic theory. If it were possible to measure the film constants with the requisite precision, we could rely on calculations of phase shift with complete confidence. Since we cannot make these film constant measurements precisely enough, it will be necessary to supplement these measurements by phase shift measurements and thus solve our problem with the theory as a guide.

Several mathematical methods are available for the solution of our problem making use of electromagnetic theory. The method discussed by Muchmore[3] making use of transmission line theory seems to offer the greatest simplicity for the iterative calculation of the phase shifts, which seems desirable for our particular problem. Leurgans[4] has given the necessary analytical equations, which we shall give in an explicit form suitable for iterative optical calculations. The general equation can be written as:

$$Y_{s+1} = \frac{\frac{n_s}{n_{s+1}} Y_s + i \tan\left(\frac{2\pi n_{s+1} t}{\lambda}\right)}{1 + i \frac{n_s}{n_{s+1}} Y_s \tan\left(\frac{2\pi n_{s+1} t}{\lambda}\right)} \tag{6}$$

where $Y_s = 1$ when $s = 1$. Here n_s refers to the index of refraction of the sth medium. If one wishes to determine φ for a reflection air to film to air, the calculation is made starting with $s = 1$ for the substrate. The reflectivity obtained will be independent of the direction of the calculation, but the phase shift is not symmetric except

when the dielectric sandwich is symmetric. Here t gives the thickness
of the film, λ the wavelength, and Y_s is a vector which is a complex
quantity in general for $s > 1$. The amplitude reflectivity R_s is given
by the expression:

$$R_S = \frac{n_s - n_{s-1} \, Y_s}{n_s + n_{s-1} \, Y_s} \tag{7}$$

In general R_s is a complex quantity. The tangent of the phase angle
produced at reflection is the ratio of the imaginary to real part of
R_s and the reflectivity R is the product of R_s and its complex conjugate.

Calculations

The theory of the phase shifts in dielectric sandwiches of equal
optical thickness predicts that a phase shift of $\varphi = \pi$ occurs at wave-
lengths for which $nt = \lambda/4$, $3\lambda/4$, $5\lambda/4$ etc. If measurements can be
made at the wavelengths for which the so called quarter wave "matches"
occur, it is immediately obvious that no phase correction is necessary
since δ_i and δ_k are both zero. Thus ideally for example, if our ideal
sandwiches consist of films of optical thickness $3\lambda_i/4$ at 5000 A and
$\lambda_k/4$ at 15,000 A, no phase correction to the measurements would be
necessary. Unfortunately the index of refraction of filming materials
is not constant with wavelength and it is not possible to make all the
films composing the dielectric sandwiches identical in optical thick-
ness. In addition, even if ideal conditions with regard to film thick-
nesses and indices of refraction did hold, it would not be possible to
find two wavelengths to measure which would fulfill the idealized

conditions. However, it should be possible to make the necessary differential corrections for the departure of our non ideal situation by obtaining information about the variation of phase shift with the pertinent variables in the neighborhood of the match points.

In Fig. 1 we have shown the reflectance curves A and B calculated for a ZnS film on quartz and a triple layer of ZnS-MgF$_2$-ZnS on the same substrate. Fig. 1, curves C and D refer to the phase variation introduced on reflection occurring respectively in the same films used to construct curves A and B. The following constants were used to construct the curves shown in Fig. 1: $n_{quartz} = 1.454$, $n_{ZnS} = 2.28$, and $n_{MgF_2} = 1.35$. The value of nt was chosen to be 4183 A. Reference to Fig. 1 D shows that $\delta/2\pi$ changes very rapidly with wavelength in the neighborhood of the $3\lambda/4$ match point and much more slowly at the $\lambda/4$ match point. However, multiplier tubes can be used as detectors in the visible which are much more sensitive than PbS detectors necessary in the infrared. Therefore, it is felt that the experimental determination of the match point in the visible can be accomplished with much more than the requisite accuracy dictated by our ability to determine the infrared match point. If the ideal set of conditions imposed to produce Fig. 1 were strictly operable, it would only be necessary to determine one of the match points to uniquely determine $\delta/2\pi$ for any wavelength. However, the assumption of constant index of refraction at all wavelengths is not strictly correct either for the filming materials or the substrate. In addition, nt for the different films cannot be made identical experimentally as has been assumed in the calculation.

In order to make a calculation more consistent with the actual composition of the thin films, we have repeated some of the first order calculations in the neighborhood of the match points allowing for dispersion and probable inequality of film thickness. The dispersion data used for ZnS were measured by Kuwabara and Isiguro[5] for thin films by means of a photometric method. Since no dispersion data for MgF_2 are available, an assumption was made that the dispersion of this substance is identical with that of LiF, which has been measured by Durie.[6] The value used for n_D for MgF_2 was 1.35, that obtained by Rood[7] from measurements on thin films. The index data used for fused quartz were taken from Sosman.[8] All index of refraction data were fitted to Cauchy dispersion formulae applying the least mean squares technique. Actual indices used were calculated from the Cauchy constants obtained for the various materials.

In Fig. 2 A we have plotted the calculated reflectance curve for a triple layer film on quartz for which the nt values were assumed to be identical for the three films. The match point for the $3\lambda/4$ film thickness was assumed to be 5578 A. Curve B Fig. 2 has been calculated assuming the first ZnS film to have its $3\lambda/4$ match point at 5578 A. The MgF_2 film and second ZnS film have their respective $3\lambda/4$ match points at 5978 A and 5363 A. This compound film yields a resultant match point identical with that of the film used to calculate curve A. Unfortunately, reference to Fig. 2 B shows that the match point, i.e. the wavelength where the phase shift on reflection is π, does not necessarily occur at the same wavelength for which the reflectance is a

maximum if the films are of unequal optical thickness. It should be pointed out that if all films are of equal optical thickness the match point and the maximum of reflectance occur at the same wavelength.

It is possible by virtue of the high reflectivity produced by the zinc sulfide layers to control very closely the thickness of those layers. However, the difficult problem in producing such a multilayer film in an ideal condition rests fundamentally on ability to make nt nominal for the MgF_2 film, since the minimum reflectance curve is very much flatter than the corresponding curves for the reflectance maxima.

Since it is only possible to measure reflectance maxima and minima during the coating process, each film will have to be examined in succession for the wavelength at which the maximum or minimum of reflectance occurs. When this data has been obtained, it will then be possible to calculate the differential phase shift with regard to an ideal composite film having equal nominal optical thickness making up its composite layers.

The distortion of the reflectance curve occasioned by non ideal film thicknesses has previously been observed experimentally by Dufour.[9] Curve C in Fig. 2 shows the calculated phase variation as a function of wavelength for the two films whose reflectance curves are A and B respectively. Within the accuracy of the calculation the phase variation proved to be identical for the two films in the neighborhood of the match point.

We have laid the theoretical ground work for the determination of wavelength standards in the infrared with respect to known wavelengths in the visible part of the spectrum by a strictly interferometric method.

It has been shown that dielectric films can be used for the interfero-
meter plate coatings and the large phase correction with wavelength
eliminated except for differential corrections by making measurements
in the neighborhood of the two match points at which the phase shifts
are identical. The accuracy obtainable by this method should depend
upon the exactness with which it is possible to determine the wavelengths
at which the effective maximum and minimum reflectances of the etalon
plates occur. We are not in a position at present to predict the probable
error in wavelength obtainable by the method discussed above, since
it will be necessary to prepare two interferometer plates with identical
coatings in order to obtain the maximum sensitivity in the determination
of the match points.

We have presumed in this discussion that measurements will have
to be made in the most ideal manner using parallel light incident on
the interferometer. In addition, since it will be necessary to use
energy measuring devices for detectors, suitable corrections will have
to be applied to the observed maxima, as has been demonstrated by Rank
and Bennett in the previous paper.

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Legends for figures

Fig. 1   Curves A and B show the theoretical reflectivity plotted
         vs. wavelength for one ZnS film and a triple layer
         ZnS - MgF$_2$ - ZnS film on a quartz substrate.   Curves
         C and D respectively show the phase variation intro=
         duced on reflection from air to film to air for these
         films.   Constant indices were assumed and the optical
         thickness of all films was chosen to be 4183 A.

Fig. 2   Curves A and B show the theoretical reflectivity plotted
         vs. wavelength for two triple layer ZnS - MgF$_2$ - ZnS
         films of equal and unequal optical thickness but the
         same resultant match point on quartz substrate.   Curve C
         shows the phase variation on reflection from air to
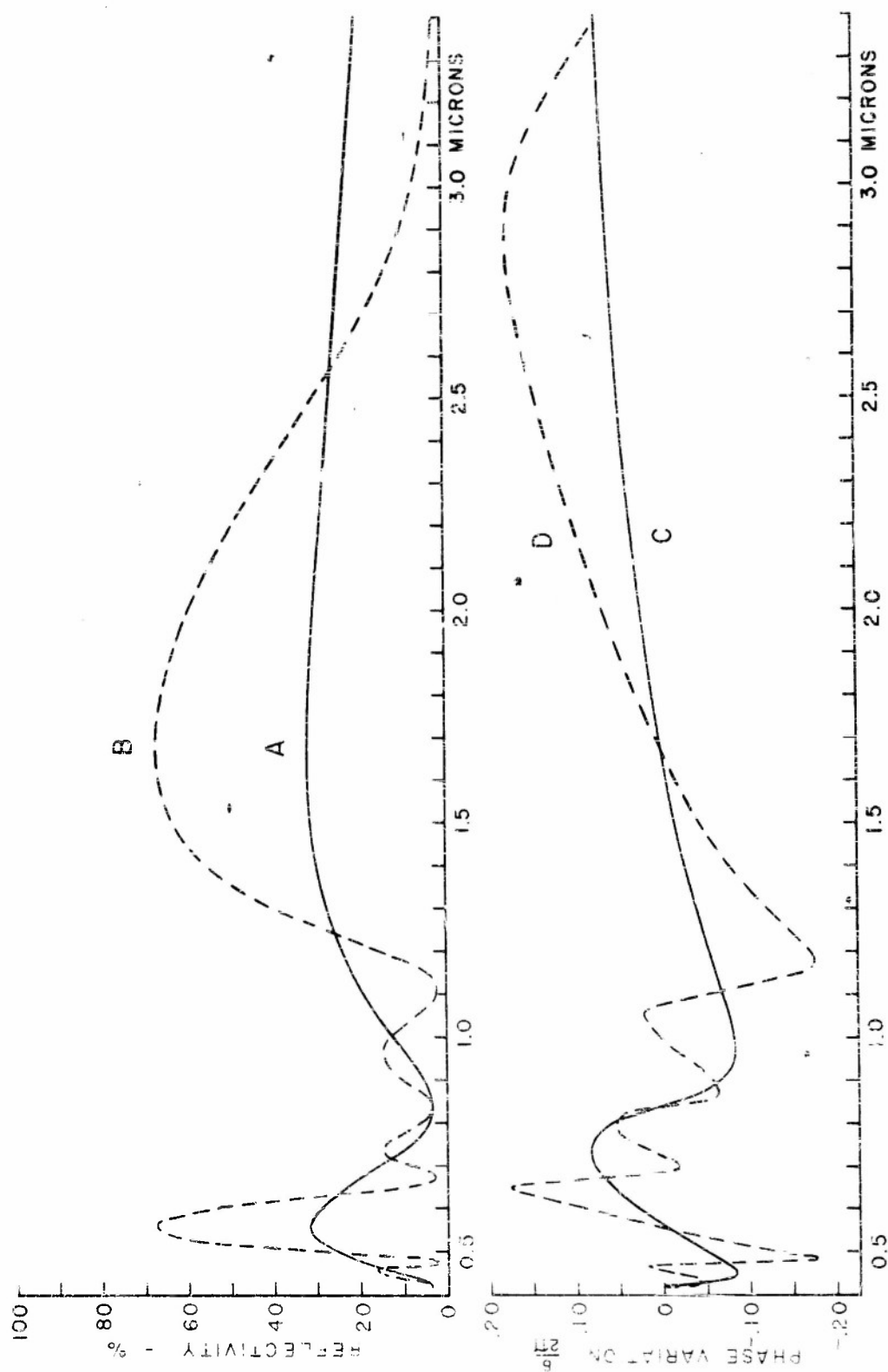   film to air common to the resultant films.
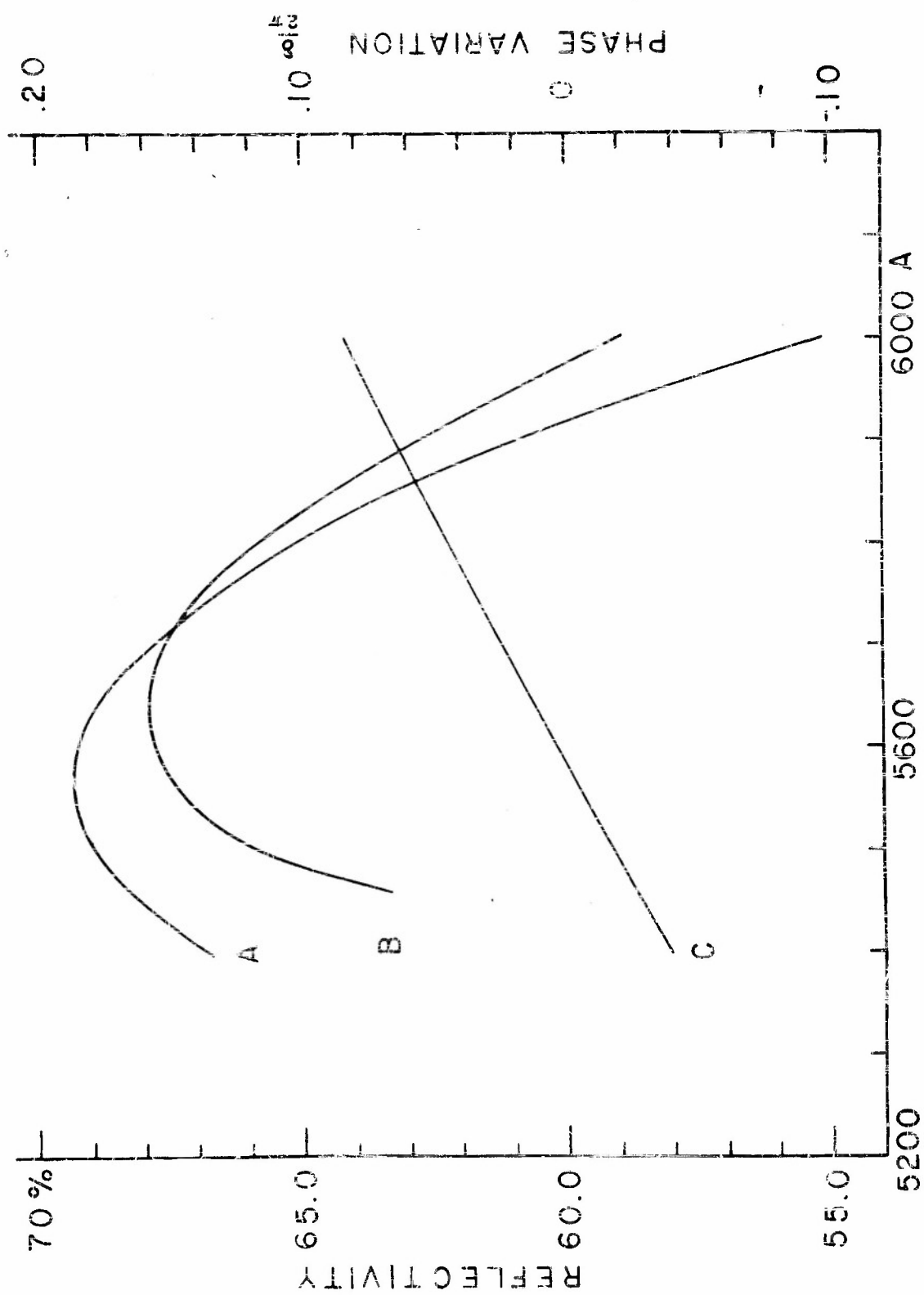
FIGURE I

FIGURE 2

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